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ENGINEERING ANALYSIS
OF
EMISSIONS CONTROL TECHNOLOGY
FOR
SULFURIC ACID MANUFACTURING PROCESSES
VOLUME 2
LITERATURE SEARCH

FINAL REPORT UNDER CONTRACT CPA 22-69-81
FOR
DIVISION OF PROCESS CONTROL ENGINEERING
NATIONAL AIR POLLUTION CONTROL ADMINISTRATION
PUBLIC HEALTH SERVICE
U.S. DEPARTMENT OF HEALTH, EDUCATION & WELFARE

MARCH 1970
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157

CONTENTS

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CONTENTS

VOLUME 2 - LITERATURE SEARCH

PART I

INTRODUCTION

PART II

REMOVAL AND RECOVERY OF SULFUR OXIDES FROM SULFURIC ACID PLANT TAIL GASES

PART III

SULFURIC TRIOXIDE AND SULFURIC ACID MIST EMISSIONS AND THEIR CONTROL

PART IV

REMOVAL OF NITROGEN OXIDES FROM CHAMBER AND MILLS - PACKARD SULFURIC ACID PLANT TAIL GASES

PART I

I

INTRODUCTION

This literature search forms a part of the final report under contract CPA 22-69-81 entitled: "Engineering Analysis of Emissions Control Technology for Sulfuric Acid Manufacturing Processes." The search is divided into three bibliographies covering the areas and periods described below.

Removal and Recovery of Sulfuric Oxides from Sulfuric Acid Plant Tail Gases

This bibliography covers a search of Chemical Abstracts, 1955-1967, current technical journals and government publications. Also included are references to waste gases such as power plant stack gases and residual gases from the Claus process, since these have similar compositions to sulfuric acid plant tail gases, and may provide useful information applicable as well to H_2SO_4 plants.

Sulfur Trioxide and Sulfuric Acid Mist Emissions and Their Control

This bibliography covers a search of Chemical Abstracts 1907-1967, current technical journals and government publications.

Removal of Nitrogen Oxides from Chamber and Mills - Packard Sulfuric Acid Plant Tail Gases

This bibliography covers a search of Chemical Abstracts 1907-1968, and current technical journals available in Chemico's Library. The bibliography also includes reference to the removal of nitrogen oxides from waste gases in general.

PART II

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A BIBLIOGRAPHY OF SULFUR DIOXIDE REMOVAL AND RECOVERY FROM WASTE GASES AND SULFURIC ACID PLANT TAIL GASES, EXCLUDING THE LIMESTONE AND DOLOMITE INJECTION PROCESSES, 1953-1968, WITH ABSTRACTS

TABLE OF CONTENTS
(Subject Index)

I. Data on SO_2 emissions:
  a) From stacks of coal-burning furnaces (2, 4, 6, 184)
  b) From stacks of oil-burning furnaces (2, 4, 6)
  c) From sulfuric acid plants (1, 2, 3, 4, 5, 7, 184)

II. Toxicity and tolerance of SO_2 in atmosphere (8 to 11, 17)

III. Absorption of SO_2 in water (12 to 23, 93)

IV. Absorption of SO_2 in inorganic aqueous salt solutions:
  a) Ammonia (24 to 29)
  b) Ammonium sulfite (24, 29, 30 to 58, 93)
  c) Ammonium phosphate (59)
  d) Basic aluminum sulfate (93)
  e) Beryllium sulfate (60)
  f) Potassium carbonate (61)
  g) Potassium sulfite (89)
  h) Selenious acid (62, 63)
  i) Sodium carbonate (64 to 71)
  j) Sodium formate (71)
  k) Sodium hydroxide (69, 73 to 78)
  l) Sodium phosphate (79)
  m) Sodium sulfite (80 to 88)
  n) Sodium thiosulfate (90)
  o) Others (91)

Table of Contents - Page 2.

V. Aqueous slurries:
  - a) Activated carbon (92)
  - b) Basic aluminum sulfate (93)
  - c) Limestone or lime (32, 69, 94-100, 213)
  - d) Magnesium oxide (101 to 108)
  - e) Manganese compounds (106, 109 to 117, 171, 172)
  - f) Red mud (118, 119)
  - g) Zinc oxide (120 to 124)

VI. Sorption by solid materials:
  - a) Activated carbon (125 to 133).
  - b) Alumina (134)
  - c) Alkalized alumina (135 to 140, 213)
  - d) Copper Oxide-alumina (140 a, b)
  - e) Manganese oxides (131, 141 to 148)
  - f) Sodium carbonate and bicarbonates (149, 150)
  - g) Zeolite (151, 181a)

VII. Molten salts (152 to 154)

VIII. Aqueous solutions of organic compounds:
  - a) Amines (67, 155, 159)
  - b) Dimethylformamide (160)
  - c) Dimethyl sulfoxide (161)
  - d) Glycol (162)
  - e) Glyoxal (163)
  - f) Glyoxylic acid (164)
  - g) Xylidine (165 to 168)
  - h) Others (93, 162, 165 to 170)

IX. Oxidation of SO_2 to SO_3
  - a) Oxidation in aqueous media (171 to 174)
  - b) Oxidation with ozone (115, 116, 175 to 180)

Table of Contents - Page 3.

c) Oxidation on ion exchange resins (181, 181a)
d) Catalytic oxidation followed by absorption (182 to 199)

X. Removal of SO_2 by reduction
a) Reduction with H_2S (200-202)
b) Other catalytic reduction of SO_2 (203)

XI. Chromatographic separation (204 to 206)

XII. General reviews and economic aspects (83, 89, 126, 138, 152, 155, 166, 185, 192, 207 to 220)

XIII. Bibliographies (221 to 223)

A BIBLIOGRAPHY OF SULFUR DIOXIDE REMOVAL AND RECOVERY FROM WASTE GASES AND SULFURIC ACID PLANT TAIL GASES, 1955-1967, WITH ABSTRACTS

1. Anon. - 1967. New U.S. Cost Study on sulfur removal. Sulphur (London) No. 68, Jan.-Feb. 1967, p. 34.

According to Garney, J.R., pres-/Bituminous Coal Research, Inc., at the Coal Convention of the Am. Min. Cobgress at Pittsburgh, Pa., when coal contains 3.4% S, the stack gas contains SO_2 3000 ppm., SO_3 30 ppm by vol. With stacks 400-800 ft. high, the ground level SO_2 content in the atmosphere would be about 0.3 ppm. SO_2. But the U.S. Public Health Service has suggested a max. ground level concn. of S oxides to be 0.1 ppm. This requires a coal contg. no more than 1% S. At present, said Mr. Garney, only 10% of U.S. coal can meet this requirement.

2. Anon. -1955. Industrial air pollution. Chem. Age 73, 995-7 (Nov. 5, '55.)

A report of the Chief Inspector (in U.K.) of industrial works for 1954 is reviewed. Emission in excess of statutory limits occurred in 24 cases. Desulfurization by scrubbing was used in a number of power plants. The chamber-process H_2SO_4 plants showed an average of 1.84 grains of SO_3 per cu. ft. of effluent gas. In 15 cases, the statutory limit of 4 grains/cu. ft. was exceeded. No limits are yet laid down for the acidity of emissions from contact acid plants, except the provision of the "best possible means" of control.

3. Ludwig, J.H., & Spaite, P.W. (U.S. Public Health Service, Cincinnati, O.) Control of Sulfur dioxide pollution. Chem. Eng. Prog. 63, June 1967, p. 82-86. (Chemico reprint 2764.)

It is estimated that air pollution by SO_2 will continue to increase in the near future and will reach a peak in 1980 at a level almost twice as high as 1966. SO_2 discharged into the atmosphere in the U.S. in 1963 is given in Table 1. (See page -4a- following.)

4. National Society for Clean Air (London, England). Sulfur dioxide as an atmospheric pollutant. Report by the Tech. Comm. of the Natl. Soc. for Clean Air, London, 1965(?), 32 pp.

A survey of the SO_2 emissions into the atmosphere in Britain has been made, and possible means to minimize this emission are discussed. Table 2 shows the source of SO_2 pollution in Britain. (See page -4b- following.)

TABLE 1

Sulfur Dioxide Emission to U. S. Atmosphere in 1963

Process	Sulfur Dioxide*	
	Ton	% of Total
Combustion of coal		
Power generation (211,189,000 ton)	9,580,000	41.0
Other combustion (112,630,000 ton)	4,449,000	19.0
Subtotal	14,029,000	60.0
Combustion of petroleum products		
Residual oil, power generation	650,600	2.8
Residual oil, other combustion	3,052,000	13.1
Other petroleum products	1,115,000**	4.8
Subtotal	4,827,000	20.7
Refinery operations	1,583,000	6.8
Smelting of ores	1,735,000	7.4
Coke processing	462,000	2.0
Sulfuric acid manufacture	451,000	1.9
Coal refuse banks	183,000	0.8
Refuse incineration	100,000	0.4
	23,370,000	100.0

* A small amount of this tonnage is converted to sulfur trioxide and sulfuric acid mist before discharge to the atmosphere.
** 10,000 tons from gas included.

Note that the largest single source is the generation of electric power: 41.0% from coal combustion and 2.8% from residual oil combustion, a total of about 44%.

Table 2

Estimates of Air Pollution by Sulphur Dioxide from the Main Uses of Fuels in Great Britain in the Year 1963

Figures are in millions of tons to the nearest 0·1 million tons for quantities of fuel and to the nearest 0·01 million tons for sulphur dioxide

Fuel and Class of Consumer	*Quantity of Fuel*	*Quantity of Sulphur Dioxide discharged*
COAL		
Domestic (including miners' coal)	32·0	0·82
Electricity works	66·8	2·04
Railways	4·9	0·14
Industrial and miscellaneous	41·8	1·20
Coke ovens	23·5	0·08
Gas works	22·1	0·16
	191·1	4·44
COKE		
Domestic coke and other manufactured solid smokeless fuels	5·9	0·12
Blast furnaces	10·5	small
Industrial	9·3	0·22
	25·7	0·34
OIL		
Domestic		
Kerosene and domestic fuel oils	2·1	0·01
Industrial		
Kerosene, gas/diesel oil, fuel oils and creosote-pitch	30·8(*a*)	1·48
Road and Rail Transport		
Motor spirit, gas/diesel oil, and fuel oils	13·1	0·06
Marine Craft		
Gas/diesel oil and fuel oils	1·1	0·04
	47·1(*b*)	1·59
Overall total quantity of sulphur dioxide		6·37

Notes

(*a*) The amount of 30·8 million tons of oil is equivalent in heating value to about 52 million tons of coal, which if used for the same purposes would have produced about 1·5 million tons of sulphur dioxide.

(*b*) The amount of 47·1 million tons of oil is equivalent to about 80 million tons of coal, so that the coal equivalent of the coal and oil consumed (excluding air transport) in Great Britain in 1963 was about 271 million tons.

5. Rohrman, F.A., & Ludwig, J.H. (U.S. Public Health Service, Cincinnati, O.) Sources of sulfur dioxide pollution. Chem. Eng. Prog. 61, Sept. 1965, p. 59-63. (See table in reference 3.)

   In 1963 more than 23 million tons of SO_2 were discharged into the atmosphere of the U.S. The power plants are the chief culprits of this unfortunate situation, accounting for over 40% of the total emission.

6. Rohrman, F.A., Steigerwald, B.J. & Ludig, J.H. (U.S. Public Health Service, Cincinnati, O.) Power plant and other sulfur dioxide emissions 1940-2000. Paper presented at ASME-IEEE National Power Conference, Albany, N.Y. Sept. 19-22, 1965, 5 pp. (Chemico reprint 2925.)

   SO_2 emissions in the United States in 1963 are presented. Emissions during the period 1970-2000 are forecast. Under conditions of present control practices the emissions during the next 30 year would be as shown in Table 3.

7. U.S. Public Health Service. Atmospheric emissions from sulfuric acid manufacturing processes. U.S. Public Health Service, Environmental Health Services, Air Pollution. Publication No. 999-AP-13, 1965, 127 pp. U.S. Govt. Printing Office, Washington, D.C., $0.60. (Chemico reprint 2908.)

   U.S. has about 163 contact H_2SO_4 plants and about 60 chamber H_2SO_4 plants. The primary emidsions from the chamber plants contain SO_2 01-0.2%, N oxides (mostly NO_2) 0.1-0.2%, and H_2SO_4 mist 5-30 mg./scf. 90% of the mist is larger than 3 microns in diameter. Equipment for reducing the emissions beyond the Gay Lussac tower is rearely employed. Emissions from the contact plants contain SO_2 0.1-0.5%, SO_3 0.5 to 48 mg./scf., and H_2SO_4 mist 3-15 mg./scf. Electrostatic precipitators, glass-fiber mat or stainless steel wire mesh pads eliminate 94-99.9% of the mist, but do not remove SO_2 or dry SO_3. Some plants use the Cominco process to reduce the SO_2 content in the tail gas to about 0.03% in 2 stages of $(NH_4)_2SO_3$ scrubbing. But Cominco process does not remove H_2SO_4 mist.

8. Anon.-1969. Control of air pollution in the U.S. moved forward. Chem. Eng. 76, Feb. 24, 1969, p. 38.

   The U.S. Dept. of Health, Education and Welfare issued two air-quality criteria covering sulfur dioxide and particulates, which states that 0.1 ppm or more of SO_2 in the atmosphere over a 24-hour period, and 80 micrograms or more of particulates per cubic meter of air "may produce adverse health effects in particular segments of the population."

9. Patty, F.A. "Industrial hygiene and toxicology" Vol. II, Chap. 18, Interscience Publishers, N.Y., 1949.

   The tolerances for man for prolonged exposure have been set at SO_2 10 ppm., SO_3 1 ppm., H_2SO_4 2-10 ppm., H_2S 20 ppm., (But for vegetables and trees, especially in growing season, the SO_2 tolerance is much smaller, about 0.20 ppm. (Katz, M., & Cole, R.J. Ind. Eng. Chem. 42, 2258-2269 (1950).

Table 3

Estimated Potential for Sulfur Dioxide Pollution

Sources of Pollution	Annual Emission of Sulfur Dioxide (millions of tons)				
	1963 (10)	1970	1980	1990	2000
Power Plant Operation (coal and oil)	10.1	15.6	30.3	51.6	60.7
Other Combustion of Coal	4.5	3.9	3.2	2.6	2.1
Combustion of Petroleum Products (excluding power plant oil)	4.3	4.9	5.9	9.2	8.9
Smelting of Ores	1.7	1.8	2.1	2.3	2.5
Petroleum Refinery Operation	1.6	1.6	1.6	1.6	1.6
Miscellaneous Sources*	1.2	0.8	0.5	0.3	0.2
TOTAL	23.4	28.6	43.6	65.6	76.0

* Includes coke processing, sulfuric acid plants, coal refuse banks, and refuse incineration.

10. Squires, A.M. (College of the City of N.Y.) Air pollution: the control of SO_2 from power stacks, I-II. Chem. Eng. 74, Nov. 6, 1967, 260-8; Nov. 20, 1967, p. 133-140.

The hazards of SO_2 to health and damages to vegetables and trees are represented graphically as functions of SO_2 concentrations in atmosphere and duration of exposure. The economics of removing sulfur from fuels before burning and of removal of SO_2 from the stack gases of power stations are discussed.

11. U.S. Bureau of Mines. Engineering evaluation of processes for sulfur dioxide removal. Air Pollution Control Project report June 30, 1956, p. 8-14.

Flue gases resulting from the combustion of coal contain about 0.06% sulfur dioxide for each percent of sulfur in the coal. Sensitive plants may be damaged by concentrations exceeding 0.25 ppm. Sulfur dioxide is known to be a respiratory irritant, and at a concentration of 0.001% produces coughing. Methods which may serve to reduce the sulfur dioxide content of stack gases include coal preparation treatments and pretreatments. The cost of sulfur dioxide removal by industrial processes ranges from 1 to 2 dollars/ton of coal consumed.

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12. Anon.-1967. Further research into flue gas cleaning. Sulphur (London) No. 72, Sept-Oct. 1967, p. 29' Chem. Eng. 74, Mar. 27, 1967, p. 43.

In Kangana, Japan, SO_2 removal by absorption in plain water and sea water is being tried in a pilot plant. It is reported that with water at pH = 7, SO_2 in flue gas was reduced from 1300 ppm. down to 80 ppm. But if water has a pH of 12, the SO_2 content was decreased to 20 ppm.

13. Andrianov, A.P., & Chertkov, B.A. Ammonia recycle method for the sulfur dioxide absorption from flue gases. Khim. Prom. 1954, 394-401; C.A. 49, 4971 b (1955).

Preliminary information is reported on a process of flue gas purification from SO_2 by cooling it with water spray and neutralizing with NH_3. Among the problems yet to be solved are the corrosion of equipment and the efficiency of absorption.

14. Germerdonk, R. (Farbenfabriken Bayer AG, Leverkusen, Germany).

Scrubbing out of sulfur dioxide from flue gases. Chem.-Ing.-Tech. 37, 1136-1139; (Nov. 1965) (Chemico transl. TR-382.)

(Continued next page)

Cont'd

14. An economical method of removing SO_2 from power plant stack gas is to scrub the gas with cold water at pH of 7.0 and to drive the SO_2 out of the water by reducing its pH to 3.5 by adding H_2SO_4 and blowing with a steam-air mixture. The desorbed SO_2 may be concentrated and utilized in the manufacture of H_2SO_4 or some other product. The water is neutralized with NaOH and recycled. A process flow diagram is shown.

15. Jackson, A., & Solbett, J.M. Sulfuric acid plant tail gas treatment. Chem. & Ind. 1955, 1304-1311 (Oct. 15)

    (1) Water scrubbing (with SO_2 stripping from the pregnant water by using it as a coolant for the burner gas), (2) NH_3 soln. scrubbing, and (3) Na_2SO_3 scrubbing are described. Data are given in 8 tables. 25 references.

16. Johnstone, H.F. and Singh, A.D. Recovery of sulfur dioxide. Industrial and Engineering Chemistry, Vol. 29, No. 3, 1937, pp. 286-297.

    The absorption of SO_2 in water and 0.5 N NaOH in packed columns was investigated with respect to packing design, operating conditions, mass transfer, and heat transfer.

17. Katz, M., & Cole, R.J. Recovery of sulfur compounds from atmospheric contaminants. Ind. Eng. Chem. 42, 2258-2269 (1950).

    Methods of recovering S values from stack gases are briefly described. The tolerance of SO_2 in atmosphere for humans and for plants and vegetables are discussed. At the Battersea power station in London, England, the flue gas contains 0.02-0.05% SO_2. Scrubbing with water from Thames River followed by a scrubbing with a slurry of chalk reduced the SO_2 content to 20-50 ppm in the gas discharged into the atmosphere.

18. Kelly, F.H.C. (Electrolytic Zinc Co., Risdon, Tasmania). Design and operation of a counter current gas-scrubbing system. Proc. Australian Inst. Min. & Met. 152-153 17-39 (1949); C.A. 46, 4281 g (1952).

    Roaster gases contg. up to 5% SO_2 has been treated in a scrubbing tower through which sea water was circulated. Effluent gas contained only 0.05% SO_2. The operating variables of the scrubber have been studied. If unlimited amount of sea water is available, SO_2 in the gases can be completely removed.

19. Kettner, H. (Inst. for Water-Ground & Air-Hygiene, Dusseldorf, Germany). The removal of sulfur dioxide from flue gases. Bul. of the World Health Organization (N.Y.) 32, 421-429 (1965). (Chemico reprint 2818).

(Continued next page)

Cont'd 19. Water scrubbing of flue gas is used by the Battersea power station in London to remove 70% of the SO_2 in the flue gas. The scrubbing water is discharged into Thames River downstream of the power station. SO_2 in the scrubbing water is not recovered.

20. Mirev, D., Elenkov, D., & Balarev, K. Rate of absorption of pure gases. Compt. rend. acad. bulgare sci. 14, 263-6 (1961); C.A. 55, 24135 a (1961).

Absorption rates of pure SO_2 in water were determined in wetted-wall column and in horizontal column at relative water rate of 30-100 cc/min. and gas rate of 1300 cc/min. SO_2 gas pressure was 215 mm. Hg. Results showed that change in gas velocity do not affect the rate of absorption of SO_2 in either the wetted-wall column or the horizontal column.

21. Parkison, R.V. Absorption of SO_2 from gases of low concentrations. Tappi 39, 522-7 (July 1956); C.A. 50, 13440 e (1956).

The absorption of SO_2 in water has been studied with SO_2 concn. in the gas varied from 0.5 to 1.5%. Results are given in a table and several graphs.

22. Potop, I.P. Reclaiming sulfur dioxide from waste gases. Rev-Chim (Bucharest) 13, 705-17 (1962); C.A. 58, 13485 h (1953).

Gases containing 0.76-1.4% SO_2 resp., were scrubbed with water at 25°-45°, resp. and atm. pressure. The pregnant water contained 1.625-2.3 g. SO_2 per 1. The SO_2 is desorbed by raising the water temperature.

23. Whitney, R.P. & Vivian, J.E. (M.I.T.) Absorption of sulfur dioxide in water. Chem. Eng. Progress 45, 323-337 (1949); C.A. 43, 4905 a (1949).

Exptl. results on the absorption of SO_2 in H_2O, in a packed tower, are presented. Over-all coeffs. for SO_2 absorption show all the characteristics of a system where both gas and liquid film resistances exert an appreciable effect. They increase markedly with increasing liquor rate, gas rate, and temp. With the aid of certain assumptions based upon previous absorption studies, the over-all coeffs. have been broken down

(Continued next page)

Cont'd 23. to yield values for the 2 film coeffs. The liquid film coeffs. of this study are significantly lower than those predicted for the system. As with the Cl_2-H_2O system, the explanation for this difference appears to lie in the relative rates of diffusion and hydrolysis of the SO_2 within the liquid film. Pseudoliquid film coeffs., calcd. by assuming no hydrolysis within the film, are in agreement with the predicted values.

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24. Anon. -1969. SO_2 recovery from sulfuric acid plant off-gases. Sulphur (London) No. 80, Jan.-Feb. 1969, p. 36-38, 40.

Two processes for the recovery of SO_2 from the tail gas of H_2SO_4 plants are described: I. The Czech process uses aq. NH_3 to absorb the SO_2 followed by a water scrubbing reducing the SO_2 content from 0.25% down to 0.01%. The absorbed SO_2 is liberated by adding HNO_3. The final liquid product is concentrated to give a NH_4NO_3 solution contg. some $(NH_4)_2SO_4$. The NO content in the recovered SO_2 gas is of the order of 0.05%. (Cf. Czech Pat. 100 295.) II. The Romanian process uses a solution of NH_4HSO_3 to absorb SO_2 from H_2SO_4 plant tail gas. The SO_2 in the absorbent is liberated by adding H_3PO_4 and the resultant liquid is concentrated to give a solution of NH_4 H_2PO_3.

25. Anon. -1967. German systems reclaim SO_2. Europ. Chem. News 11, Mar. 10, 1967, p. 34.

Air pollution can be minimized and sulphur dioxide conserved by incorporating into the design of sulphuric acid plants a double absorption system or a scrubbing system each developed by Chemiebau Dr. A. Zieren GmbH.

The double absorption system, which is already being used in sulphuric acid plants in Lenzing (Austria), Antwerp and Magdeburg, is claimed to reduce sulphur dioxide losses of a 330,000 ton/year plant from 4,300 ton to 1,000 ton annually.

It is equally suited to recovering sulphur dioxide from off gases having a high or low concentration of sulphur dioxide.

Water and ammonia are used for scurbbing the sulphur dioxide from the off gases in the second process, which has been incorporated in sulphuric acid plants at Rravancore, Geleen, Wesseling, Worms and Zwickau.

One virtue of the latter technique is that it can be used for recovering sulphur dioxide in the event of a failure in the steam supply putting the absorption system out of action.

Proportion of sulphur dioxide lost to the atmosphere when off gases from a 330,000 ton/year plant are purified by scrubbing is said to be reduced to 130 ton/year.

26. Bergwerksverband zur Verwertung von Schutzrechter der Kohlentechnik G.m.b.H. (Grosskinsky, O., Klempt, W., & Adelberger, A., inventors). Ammonium sulfate from gases with a low SO_2 content. Ger. Pat. 801,837, Jan. 25, 1951 (Cl. 12k. 7); C.A. 45, 8728 d (1951).

Gases contg. less than 1 vol. % SO_2 may be scrubbed with NH_4OH soln. to recover SO_2 as $(NH_4)_2SO_4$. The scrubbing soln. is maintained at pH 4-5.5 in the presence of 50-120-fold 0 excess based on SO_2. The flow ratio should be 120-200 vol. of gas per vol. scrubbing soln. which is kept at 60-65°. The SO_2 loss and NH_3 loss are, respl, 0.17% and 0.11% based on total charge. The effluent gas contains 0.001% SO_2 and 0.002% NH_3. The efficiency obtained in treating a gas contg. 0.1% SO_2 is about one-half as high as for 1% SO_2.

27. Furkert, H. & Muehlenbein, H. (to Chemiebau Dr. A. Zieren G.m.b.H. Cologne-Braunsfeld, Germany). Process for recovering sulfur dioxide and ammonia from aqueous scrubbing solution obtained from ammonia scrubbing of gases containing sulfur oxides. U.S. Pat. 3 321 275 (Cl. 23-178) May 23, 1967. (Germ. appl. Dec. 3, 1963).

SO_2 in gases is removed by scrubbing with a solution of NH_3. The $(NH_4)HSO_4$ and $(NH_4)_2SO_4$ formed during the process is separated and decomposed at 200°F. to recover NH_3 which is recycled.

28. Klimecek, R., Kana, B., Mikulsky, R., & Jara, V. Removal of sulfur oxides from industrial gases. Czech. Pat. 111 472 (Cl. C 02c) July 15, 1964 (appl. Dec. 8, 1962); C.A. 62, 4948 b (1965).

SO_2 is absorbed in aq NH_3. The resulting NH_4HSO_3 is oxidized to $(NH_4)_2SO_4$. The latter is treated ZnO $Zn(OH)_2$ or $ZnCO_3$ to expel the NH_3. The expelled NH_3 is absorbed in water and recycled to the gas scrubber.

29. Slack, A.V. (TVA) Air pollution: The control of SO_2 from power stacks. III. Processes for recovering SO_2. Chem. Eng. 74, Dec. 4, 1967, p. 188-196.

The recovery of SO_2 in gases by absorption and desorption with an aq. soln. of NH_3 was applied by Cominco in Canada to the smelter gases. Its application to flue gases on large scale was first realized in Japan with a 25Mw oil-burning power station. The system was put in operation since Oct. 1966 by Showa Denko KK. But the Showa Denko system does not involve desorption of SO_2, it converts all SO_2 to $(NH_4)_2SO_4$ which is recovered as a solid product. This simplifies the process and materially cuts down costs.

30. Anon. -1967. Czechoslovakia; desulfurization of flue gases using ammonia. Sulphur (London) No. 72, Sept-Oct, 1967, p. 24-26.

A SO_2 recovery system is in operation in Northern Bohemia, Czechoslovakia, based on absorp. with $(NH_4)_2SO_3$ soln. The installation is at the 100,000 kw power station 500,000 m^3 flue gas per h. (0^oC and 1 atm.) contg. 0.1 to 0.3 mole % SO_2 at 140^o-180^o C. The absorbers (2 in series) are operated at 50^o-60^o. In the case of single absorber the SO_2 content of the flue is usually reduced to 0.01 mole %. The reduction is more with 2 absorbers in series and the NH_3 recovery is better with 2 absorbers in series.

The pregnant soln. is acidified with H_2SO_4 to liberate in SO_2 which is sent to a H_2SO_4 plant to make the acid. The acidified soln contains $(NH_4)_2SO_4$ which is concentrated and recovered by crystallization, as a by-product.

The "re cycle" version of the process involves the recycling of an acidified soln. containing a higher acidity in order to drive out SO_2 at less expenditure of steam. Thus recycle is confined to the SO_2 desorption portion of the process. Plastics are used in making part of the equipment to circumvent corrosion.

31. Anon. -1955. SO_2 scrubber, two scrubs better than one. Chem. Eng. 62, Feb. 1955, p. 132, 134; Chem. Eng. News 33, 2148-9 (May 16, 1955).

Olin Matheison Chem. Corp's plant on the Houston Ship Channel, Tex., uses Cominco process and their own modifications. The H_2SO_4 plant (estimated capacity 600 tons/day) discharges 2,160,000 SCF gas per h. contg. 0.3% SO_2. By using $(NH_4)_2SO_3$ soln. in a 2-stage gas scrubbing system the exit gas contains 0.03% SO_2. The absorbed gas is desorbed by adding 66° H_2SO_4 to the pregnant soln. and blowing dried air through it. The effluent gas contg. a high concn. of desorbed SO_2 is combined with the feed SO_2 gas just before the drying tower. By installing this system the plant production was pushed up 20%. The cost of the equipment was $340,000 (about 17% of the total H_2SO_4 plant investment, but it is automatically operated requiring no added personnel).

32. Atsukawa, M., Nishimoto, Y., & Matsumoto, K. (Hiroshima Tech. Inst. Japan). Removal of SO_2 gas from waste gases. Mitsubishi Heavy Inds. Ltd., Tech. Rev. 2, No. 2, 51-57 (May 1965).

Four processes of removing SO_2 from waste gases which are being developed by Mitsubishi Heavy Inds. Ltd. are described with flow diagrams: (1) NH_4HSO_3 liquor process, (2) MnO(OH) slurry process, (3) milk of lime process, (4) red mud slurry process. For all these processes, an inlet gas contg. SO_2 0.1-0.2%, for the pilot plant tests was used. For processes (1) and (2) the removal efficiency was of the order of 97% and for processes (3) and (4) it was about 90%. Processes (2) and (4) required higher liquid/gas ratios.

33. Bergwerksverband zur Verwertung von Schutzrechter der Kohlentechnick G.m.b.H. (Grosskinsky, O., Klempt, W., & Adelberger, A., inventors).

Ammonium dioxide content. Ger. Pat. 801 837, Jan. 25, 1951 (Cl. 12k. 7); C.A. 45, 8728 d (1951).

Gases contg. less than 1 vol. % SO_2 may be scrubbed with NH_4OH soln. to recover SO_2 as $(NH_4)_2SO_4$. The scrubbing soln. is maintained at pH 4-5.5 in the presence of 50-120-fold O_2 excess based on SO_2. The flow ratio should be 120-200 vol. of gas per vol. scrubbing soln. which is kept at 60-65°C. The SO_2 loss and NH_3 loss are both low, i.e., 0.17% and 0.11%, resp.; for an original gas contg. 0.1% SO_2, the loses are 2.2% and 0.69%, resp.

34. Bettelheim, J., Frantisak, F., Derka, J., & Klimecek, R. Sulfur dioxide from industrial waste gases by ammonium cyclic method. Czech. Pat. 114 564 (Cl. C -016) May 15, 1965 (appl. Sept. 4, 1962); C.A. 64, 15440 a (1966)

In the process of recovering SO_2 from waste gases using $(NH_4)_2SO_3$ as the absorbent. It is specified that the waste gas is first cooled to below 45° C. The condensate separated at this temp. is used to scrub the gas to remove dust. The $(NH_4)_2SO_3$ solution is allowed to build up its $(NH_4)_2SO_4$ content until the latter compound crystallizes upon cooling. A slip-stream of this solution is then processed to recover $(NH_4)_2SO_4$.

35. Bettelheim, J., & Klimecek, R. Absorption of sulfur dioxide in an unpacked column with jets. Chem. Prumysl (Prague) 10 (6), 281-4 (1960); C.A. 61, 10338 n (1964).

The absorption kinetics of SO_2 in aq. $(NH_4)_2SO_3$ in an unpacked column with jets of the absorbent was studied. It is concluded that although there is no liquid film such as on the surface of packing elements, the diffusion resistance of the liquid to the absorption of SO_2 cannot be neglected since there is still a film of more conc. soln. of SO_2 around each liquid drop of the absorbent.

36. Burgess, W.D. (The Consolidated Min. & Smel. Co. of Can. Trail, 1 B.C.) So_2 recovery process. Chem. in Can. 8, No. 6, 116-120 (1956); cf. U.S. Pat. 2 862 789 (1958).

At Trail at different times there was the necessity of recovering SO_2 from gases contg. about 1% SO_2. The process which has been developed and used for many years uses an aq. soln. of $(NH_4)_2SO_3$ + $(NH_4)HSO_3$ to absorb SO_2. Aq. NH_3 is continuously added to that soln. to maintain its absorptive power. A portion of this soln. is acidified to recover SO_2 in the pure form. The SO_2 is either fed to the gas in the H_2SO_4 plant or

(Continued next page)

Cont'd 36. liquified and sold. The acidified soln. eventually builds up in $(NH_4)_2SO_4$, which is crystallized and separated as a by-product. The mother liquor is recycled after correction of pH value by adding aq. NH_3. Material balance and heat balance are tabulated.

37. Chertkov, B. A. p-Phenyldiamine as an inhibitor of oxidation of ammonium sulfite-bisulfite solution. Zhur-Prikl. Khim. 32, 952-960 (1952); C.A. 53, 15499 c (1959).

Oxidation of dust-free $(NH_4)_2SO_3$ / NH_4HSO_3 solns. with air was reduced several-fold by the presence of 0.5-3.0 g./l. of p-phenyldiamine. The effect of the latter compd. is not diminished in the presence of 0.25 M thiosulfate. However the effectiveness of p-phenyldiamine as an oxidation inhibitor is impaired by a deficiency of NH_4OH. There is an optimum SO_2/NH_3 ratio for the circulating soln., which is about 0.75. When this ratio is larger than 1.0, oxidation of SO_2 became rapid after 200 h. of operation. The presence of fly-ash in the flue gas also impairs the effectiveness of p-phenyldiamine.

38. Craxford, S.R., Poll, A., & Walker, J.S. Recovery of sulfur from flue gas by the use of ammonia. J. Inst. Fuel 25, 13-14 (1952); C.A. 46, 2267 d (1952); cf. Trans. Inst. Chem. Engrs. (London) 23, 43-51 (1945).

In the Simon-Carves process of scrubbing flue gas with NH_3 soln., the chief difficulty was the proper control of the concn. of the scrubbing soln. It was found later that the presence of $MnSO_4$ or Fe oxide stabilizes the compn. of the soln. The introduction of the electrical-conductivity vapor-pressure recorder (Brit. Pat. 633,627, Mar. 18, 1950) also helped in maintaining the proper composition so that the NH_3 loss as vapor was at the min. and SO_2 removal was 99%. The scrubbed flue gases contained only 0.005% SO_2. The spent liquor was treated in an autoclave at 190° with H_2SO_4. Elemental S and $(NH_4)_2SO_4$ were produced. On the basis of results from the 1000 cu. ft. per hr. plant, a 25,000 cu. ft. per hr. plant was built and is now in operation at the Fuel Research Station (in England).

39. Edge, H.A. (to Imp. Chem. Inds., Ltd., England) Recovery of SO_2. U.S. Pat. 2 589 684, Mar. 18, 1952.

The gas contg. SO_2 is scrubbed with an aq. soln. of $(NH_4)_2SO_3$ and NH_4HSO_3 in which the SO_2 is absorbed. The SO_2 may be liberated by adding HNO_3 in excess.

40. Ganz, S.N. Kuznetsov, I.E., & Podgaiko, V.V. Sulfur dioxide removal from gases to obtain ammonium sulfate. Khim. Teckhnol. Resp. Mezhvedomstv. Nauchn.-Tekhn. Sb. 1965 (2), 47-52 (in Russian); C.A. 65, 14896 c (1966).

    The gas contained less than 0.25% SO_2, and the scrubbing soln. was a strong $(NH_4)_2SO_3$ soln. containing less than 1% free NH_3. This soln. had a capacity of absorbing 580 g. SO_2 per liter of soln. This is about 800 times better than plain water at 25°. In the presence of air or O_2, the turbulence of circulation caused oxidation of $(NH_4)_2SO_3$ to $(NH_4)_2SO_4$ which was recovered as a fertilizer.

41. Gerrard, J.S. (to Simon-Carves Ltd., England). Production of ammonium sulfate. U.S. Pat. 3 186 792; 3 186 802 (Cl. 23-119; Cl. 23-260) June 1, 1965 (appl. Mar. 2, 1961.)

    The $(NH_4)_2SO_3$ liquor from the scrubbing column for the removal of SO_2 from waste gases is acidified with H_2SO_4 and heated under pressure in the presence of air to convert the $(NH_4)_2SO_3$ to $(NH_4)_2SO_4$ which is subsequently concentrated and recovered by crystallization.

42. Hien, L.B., A.B. Phillips, and R.D. Young. Recovery of Sulfur Dioxide from Coal Combustion Stack Gases. Chapter 15. In Problems and Control of Air Poll'n. New York, Reinhold, 1955, p. 155-169. DLC (TD883.15, 1955)

    This report discusses data obtained in pilot plant studies of the recovery of sulfur dioxide, in usable form, from coal combustion gases. The sulfur dioxide was absorbed in ammonia solution. The major variables studied were recirculation rate, pH, and concentration of the scrubbing liquor and the depth of packing and gas velocity in the scrubber. These studies were made at the laboratories at Wilson Dam, Alqbama as a part of work conducted by TVA to evaluate the emissions of sulfur dioxide from steam plants so as to identify any needed controls."

43. Jara, V., Klimecek, R., Kordik, E., & Bettelheim, J. Recovering sulfur dioxide from combustion gases. Czech. Pat. 99 875, June 15, 1961 (appl. Sept. 3, 1959); C.A. 58, 2190 g (1963).

    The hot flue gas is first cooled by contacting mineral oil. The cooled gas is scrubbed with aq. $(NH_4)_2SO_3$. The pregnant soln. is regenerated by heat which comes from direct mixing of hot oil used in cooling the gas. The oil may be filtered periodically to remove fly-ash.

44. Johnstone, H. F. (Univ. of Ill.) Recovery of sulfur dioxide from waste gases. Ind. Eng. Chem. 29, 1396-8 (Dec. 1937).

Data is given on the effect of solvent concentration upon capacity and steam requirements of ammonium sulfite-bisulfite system of SO_2 recovery from dilute gases. The optimum concn. of $(NH_4)_2SO_3$ for min. steam consumption has a value less than one-half of the concn. of the satd. salt soln. This optimum value is a function of SO_2 concn. in raw gas and of operating conditions.

45. Johnstone, H. F. (to Texas Gulf Sulfur Co.) Recovery of sulfur dioxide from waste gases. U.S. Pat. 2 676 090; Apr. 20, 1954; C.A. 48, 11018 b (1954).

The gases contg. SO_2 is scrubbed with an aq. soln. of $(NH_4)_2SO_3$. A portion of the pregnant scrubbing soln. is acidified with H_2SO_4 to liberate SO_2 after which the liquor is concentrated to recover $(NH_4)_2SO_4$. The remainder of the pregnant scrubbing solution is heated to drive out SO_2, cooled again and returned to the scrubbing column.

46. Johnstone, M. F., & Singh, A. D. (to Commonwealth Edison Co., Chicago, 121). Process for recovering sulfur dioxide from waste gases. U.S. Pat. 2 161 055 (Cl. 23-178). June 6, 1939 (appl. Mar. 24, 1937); C.A. 33, 7500 (b) (1939).

An arrangement of app. is described, and a soln. of $(NH_4)_2SO_3$ and NH_4HSO_3 to absorb the SO_2 therein, preheating the soln. contg. absorbed SO_2, introducing the heated soln. into a regenerator in contact with steam, condensing the water in the vapors issuing from the regenerator, bringing the vapors into contact with a portion of the condensate, combining the portion of condensate with the remainder of the condensate, and returning all of the condensate to the regenerator at a point below the level of the regenerated soln.

47. Johnstone, H. F. & West, Jr., W. E. (to Texas Gulf Sulfur Co.) Recovery of sulfur dioxide from gases and production of ammonium sulfate. U.S. Pat. 2,810,627, Oct. 22, 1957; (CCC Pat. Dept.)

A gas mixt-contg. SO_2 is scrubbed with an aq. solution of NH_3 in a 3-stage counter-current system from which the scrubbing liquor is withdrawn and oxidized by blowing air through it in another 3-stage countercurrent system, where the $(NH_4)_2SO_3$ is converted into $(NH_4)_2SO_4$ which is subsequently recovered by crystallization.

48. Klimecek, R., Kana, B., Mikulsky, R., & Jara, V. Removal of sulfur oxides from industrial gases. Czech. Pat. 111 472 (Cl C 02c) July 15, 1964 (appl. Dec. 8, 1962); C.A. 62, 4948 b (1965).

After absorbing the SO_2 in aq. $(NH_4)_2SO_3$ the pregnant soln. is treated with H_2SO_4 to liberate SO_2 in a conc. gas. The $(NH_4)_2S0_4$ left in the aq. soln. is treated with ZnO, $Zn(OH)_2$ or $ZnCO_3$ to liberate NH_3 which is absorbed in H_2O. The NH_3 soln. is recycled to the SO_2 absorber. The $ZnSO_4$ is recovered as a by-product.

49. Klimecek, R., Skrivanek, J., & Battelheim, J. (Ustinad Labem, Czech.) Desulfurizing flue gases. Staub Reinhaltung Luft 26 (6), 235-8 (1966) (in German); C.A. 65, 14897 d (1966).

After comparing the various processes of removing SO_2 from flue gases, the sulfite process was considered the most advantageous. A packed column for this process was designed.

50. Kohl, A.L., & Riesenfeld, F.C. (The Fluor Corp.) Gas purification. Chem. Eng. 66, June 15, 1959, 125-178.

SO_2 is absorbed, according to Cominco process, in a soln. of $(NH_4)_2SO_3$. The latter is treated with H_2SO_4 to cause SO_2 to desorb leaving behind $(NH_4)_2SO_4$ which is recovered by crystallization.

51. McCabe, L.C. Atmospheric pollution. Ind. Eng. Chem. 43, No. 8, 83A, (1951).

The success of the Simon-Carbes process (Bri. Pat. 525,883 (1940), and 633,627, (1949) depends upon close control of the soln. compn. which consists of $(NH_4)_2SO_4$ 28-34%, $(NH_4)_2SO_3$ 0-6%, NH_4HSO_3 0.75-5% and $(NH_4)_2S_2O_3$ 4-11%. In order to keep $(NH_4)_2SO_3$ within limits the presence of an oxidizing catalyst is necessary; $MnSO_4$ or $Fe(OH)_3$ may be used for this purpose.

52. Office National Industrial de l'Azote (Cluzel, J., inventor). Fixation and recovery (as ammonium sulfate) of waste sulfur dioxide in industrial effluent gas. Fr. Pat. 1 388 690 (Cl. C 016, c, F 23j) Feb. 16, 1965, (appl. Apr. 29, 1963); C.A. 63, 3930 c (1965).

In the recovery of $S0_2$ with aq. $(NH_4)_2S0_3$ as absorbent, the latter is maintained at pH 5.3-5.7 by constantly adding NH_3. The gas fed to the absorber contains 0.2-0.6% $S0_2$, and the gas coming out of the absorber contains less than 0.02% $S0_2$. The pregnant absorbent contains $(NH_4)_2S0_4$ 134.5 g., $(NH_4)_2S0_3$ 52.9 g., NH_4HS0_3 141.7 g. per liter. A slip-stream of the pregnant absorbent is treated with H_2S0_4 to pH 1.5 to liberate $S0_2$ with the aid of a strong current of air. The $S0_2$ free liquor is evaporated to a concentration at which $(NH_4)_2S0_4$ crystallizes upon cooling. The $(NH_4)_2S0_4$ is then recovered as a solid product.

53. Petersen, H. Removal of sulfur dioxide from industrial gases. Neth. Pat. Appl. 6516 530 (Cl. C Olb) June 20, 1966 (Ger. Appl. Dec. 19, 1964; Apr. 28, 1965); C. A. 66, 4549 y (1967).

SO_2-contg. gases are mixed with NH_3 and water vapor and sprayed with an aq. soln. of $(NH_4)_2SO_3$ or NH_4HSO_3 to sep. the formed $(NH_4)_2SO_3$ fog from the gas stream in a 2-step mech. separator of the Petersen type, having a pressure drop of 80-350 mm. water column. The treated gases contain <0.02 vol. % SO_2. In the 1st step of the separation, gases contg. 5-10 g. SO_2 (and some SO_3)/m^3 and having a temp. of 50-60° are together with steam brought into contact with $(NH_4)_2SO_3$ or NH_4HSO_3 soln. at 30-40° and a pH of 4.6-5.4 to remove ~50% of the SO_2. The sulfite soln. is recirculated after addn. of H_2SO_4 in a degasifier to drive out the SO_2 while elevating the temp. 3°, and sepg. solid $(NH_4)_2SO_4$ in a classifying crystallizer while decreasing the temp. 3°. By using a 2-step degasifier pure SO_2 gas can be obtained. In the 2nd step of the separation, the gases together with NH_3, air, and steam are sprayed with sulfite soln., which is recirculated by a classifying crystallizer during cooling by 3°. For each m.^{3} starting gas, 1-4 g. steam is used. Solid $(NH_4)_2SO_3$ is obtained without evapg. the sulfite soln., while comparatively little NH_3 is used.

54. Popovici, N., Potop, P., Brindus, L., & Anghel, P. Design of an installation for retaining of SO_2-containing residual gases in a plant of complex fertilizers, under economically advantageous conditions. Rev. Chim. (Bucharest) 18, (1), 40-41 (1967) (in Romanian); C. A. 66, 115 001 f (1967).

The tail gas from H_2SO_4 plants are scrubbed with a solution of $(NH_4)_2SO_3$ which absorbs SO_2. The pregnant solution is treated with dil. H_3PO_4 and by blowing air through the acidified solution, a gas containing 10-15% SO_2 is recovered. The acid solution is sent to the H_3PO_4 plant or to the phosphate fertilizer plant. A high rate of tail gas flow through the scrubber favors absorption coeff. The mist of the $(NH_4)_2SO_3$ solution created by this high flow rate is recovered by adding a plain-water scrubbing column.

55. Simon-Carves Ltd. Recovering $(NH_4)_2SO_4$. Brit. Pat. 1 031 724 Europ-Chem. News 9, July 22, 1966, p 44. cf. Belg. Pat. 632 077, Sept. 2, 1963 (Brit, Appl. June 18, 1962); (C. A. 60, 12920 d (1964).

An apparatus is specified for the oxidation of ammoniacal solns. contg. xoides of S washed out of combustion gases to yield $(NH_4)_2SO_4$.

56. Vasilenko, N. A. Ammoniacal-acid methods for enriching weak sulfur dioxide gases with nitric and phosphoric acids or their manufacture. Bolshoi Dzhezkazgan Dobycha; Pererabotka Rud. Sb. 1963, 434-443; C. A. 61, 3958 g (1964).

The $S0_2$ in gases is absorbed in aq. $(NH_4)_2S0_3$. The pregnant soln. is treated with $HN0_4$ or H_3P0_4 to liberate the $S0_2$, thus avoiding the use of H_2S0_4. A byproduct of NH_4N0_3 or $(NH_4)_2HP0_4$ is produced.

57. Volgin, B.P., & Maron, F.S. Absorption of carbon dioxide and sulfur dioxide in Venturi scrubber. Soobshcheniya o Nauch-Tekh. Rabot., Nauch. Inst. Udorbren. & Insektofungisidov 1958 No. 6-7, 118-137; C.A. 55, 10995 c (1961).

The results of expts. on the absorption of CO_2 by a Na_2CO_3 soln. and SO_2 by solns of $(NH_4)_2SO_3$-NH_4HSO_3 and Cr_2O_3 are cited. The Venturi scrubber can be used successfully for absorption of easily sol. gases at high concn. in a gaseous mixt. Of practical interest are the absorption of SO_2 by a soln. of $(NH_4)_2SO_3$-NH_4HSO_3 and of SO_3 by H_2SO_4. A high percent recovery is attained by absorption in several steps. With absorption of difficultly sol. gases, an increase of the gas velocity into the throat has more effect than an increase of the sp. consumption of liquid, but with absorption of easily sol. gases an increase of sp. consumption has more effect. During the process of absorption, the sp. consumption of liquid must be several times greater than for dust collecting. The concn. of the absorbable component in the gaseous mixt. influences the degree and coeff. of absorption considerably.

58. Woollam, J.P.V., & Jackson, A. Removal of oxides of sulfur from exit gases. J. Soc. Chem. Ind. 27, 43-51 (1949); Trans. Inst. Chem. Eng. 23, 43-51 (1945); C.A. 43, 1882 e (1949).

Gases contg. S vapor and S oxides are scrubbed with an aq. soln. of $(NH_4)HSO_3$, $(NH_4)_2SO_3$ and $(NH_4)SO_4$ at pH 5-7. The solution is periodically reinforced by adding NH_4OH. A portion of the pregnant soln. is autoclaved to convert SO_3 into SO_4.

Some elemental S is also formed in the autoclave. The latter and $(NH_4)_2SO_4$ are removed and the mother liquor is reused as scrubbing soln.

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59. Averbukh, T.D., Bakina, N.P., & Telepneua, A.E. Ammonia-phosphate method of sulfur dioxide enrichment. Trudy Ural. Nauch.-Issledovatel. Khim, Inst. 1958, No. 7, 150-170; C.A. 55, 7772 a (1961).

The recovery of SO_2 by absorption and desorption in aq. solns. may be carried out with $NH_4H_2PO_4$ solns. as well as with NH_4HSO_3 solns. The $NH_4H_2PO_4$ may be more expensive and the process may consume more steam, but there is less oxidation of SO_2 to SO_3 in the $NH_4H_2PO_4$ soln.

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60. S.A. des manufs. des glaces et prod. chim. de Saint-Gobain, Chauny et Cirey. Recovery of sulfur dioxide. French Pat. 974 179, Feb. 19, 1951; C.A. 46, 11608 c (1952).

SO$_2$ is absorbed in an aq. soln. of basic Be sulfate from which SO$_2$ is recovered by heating in vacuo. A soln. contg. BeSO$_4$ 4H$_2$O 435 g. /l., and BeO 109 g. /l. will absorb 186 g. SO$_2$ per l. of soln. at 20^o from a gas contg. 4% SO$_2$, or 196 g. SO$_2$ from a gas contg. 7% SO$_2$. The BeO used in this soln. is less than that required to saturate the soln. To eliminate the small amount of H$_2$SO$_4$ formed in the process, CaO, BaO or similar oxides may be added. Basic Al sulfate may be added to the Be soln.

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61. Bodoni, D. (to Bodoni & Co. C.m.b.H.) Recovery of carbon dioxide and sulfur dioxide from combustion gases. Austrian Pat. 174,896 May 11, 1953; C.A. 47, 7780 f (1953).

Gases contg. CO$_2$ and SO$_2$ are scrubbed with an aq. soln. contg. N (O Et)$_3$, NH$_2$ (OEt) and K$_2$CO$_3$ in the ratio 2:2:1 in which the CO$_2$ and SO$_2$ dissolves. The pregnant soln. is regenerated by heating to liberate CO$_2$ and SO$_2$. Recoveries of 95-98% of the CO$_2$ and SO$_2$ in the gases can be made.

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62. Badische Anilin-& Soda-Fabrik A.G. (Wolf, H., Goesele, W., & Schachemeier, G., inventors). Removal of sulfur dioxide from exhaust gases. Ger. Pat. 1 204 770 (Cl. F 23j) July 3, 1963 (appl. Nov. 11, 1963); C.A. 64, 5671 b (1966).

The removal of S0$_2$ by the H$_2$Se0$_3$ process is specified. An example is given: 360 liters of waste gas contg. 0.2% S0$_2$ was scrubbed with 1.31 liters of 30% H$_2$S0$_4$ contg. 2.5% Se0$_2$ by wt. in Venturi scrubber at a liquid velocity of 256 liters/h. In 2 h. the Se (3.25 g.) ppt. was filtered off. The H$_2$S0$_4$ increased in concentration. A slip stream corresponding to 5.75 q H$_2$S0$_4$ was removed and replaced with water. The Se is oxidized with air to Se0$_2$ and returned to the scrubbing soln.

63. Norddeutsche Affinerie (Emicke K., inventor). Removal of sulfur dioxide from flue gas. Belg. Pat. 665 484 Oct. 1, 1965 (Ger. Appl. June 18, 1965 (Ger. Appl. June 18, 1964); C.A. 64, 19041 a (1966).

Flue gas is first cleaned of dust with an electrostatic precipitator. It is then scrubbed with an aq. soln. contg. H$_2$Se0$_3$ 42 g/l and H$_2$S0$_4$ 77 g/l. The reaction: $2S0_2 + Se0_2 \rightarrow 2S0_3 + Se$ takes place. The Se is filtered off and processed to regenerate H$_2$Se0$_3$. A slip stream of aq. soln. is concentrated to recover H$_2$S0$_4$.

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64. Blasinski, H., & Ignaczak, W. (Politech. Lodz. Poland). Absorption of sulfur dioxide by sodium carbonate aq. soln. from a gas mixture (air-sulfur dioxide). Przemysl Chem. 45 (7), 374-8 (1966) (in Polish); C.A. 65, 14876 a (1966).

Air contg. 0.1775-0.7880% SO_2 was scrubbed in a packed column with a spray of aq. Na_2CO_3 at the top. The removal of SO_2 was 90.5-99.9% complete.

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65. Fleming, E.P. & Fitt, T.C. (to Am. Smel. & Ref. Co.) Sulfur dioxide recovery. U.S. Pat. 2 399 013 Apr 23, 1946; Brit. Pat. 598 283 Feb. 13, 1948; C.A. 40, 7538 (5) (1946); cf. U.S. Pat. 2 295 587 Sept. 15, 1943; C.A. 37, 1234 (3) (1943).

The SO_2 in a gas is absorbed by anhy. dimethylaniline (DMA) so that the effluent gas still contains a small amount of SO_2; the effluent gas is next scrubbed with an aq. soln. of Na_2CO_3 to remove the remaining SO_2. The residual gas containing DMA vapor is scrubbed with aq. H_2SO_4. The 3 scrubbing solns. are separately regenerated so as to recover pure SO_2, and the solvent. The latter is separated from the H_2SO_4 soln. by distillation.

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66. Jara, V., Bettelheim, J., & Skrivanek, J. Regenerating absorption solution used for trapping sulfur dioxide from industrial refuse exhalations. Czech. Pat. 106 240 Jan 15, 1963 (appl. Nov. 12, 1961); C.A. 60, 6524 f (1964).

The SO_2 contg. gas is scrubbed with aq. Na_2CO_3 which is transformed to $NaHSO_3$ by the SO_2. The SO_2 is liberated from $NaHSO_3$ by adding H_2SO_4. The soln. is neutralized with Na_2CO_3, and Na_2SO_4 is recovered in solid form. The Na_2SO_4 is reduced with coal or coke at 600°-1100° forming amolten Na_2S. The Na_2S is dissolved in water. The water soln. is contacted with CO_2 to liberate H_2S. The H_2S and recovered SO_2 are put through the Claus process to recover elemental S. The Na_2CO_3 soln. is recycled.

67. Johnstone, H.F., et al. (Univ. of Ill.) Recovery of sulfur dioxide from waste gases. Ind. Eng. Chem. 30, pp. 101-9 (1938).

Fig. 2 shows the capacity of Na_2SO_3-$NaHSO_3$ solutions for recovery of SO_2 from gases contg. 0.3% SO_2 at absorption temps. of 35°, 45° and 55° resp., and desorption temps. of 70°, 80°, 90°, 100° and 120°. The capacity is defined as the difference between SO_2 concn. in solution leaving absorber and that from the regenerator for a constant concn. of a base, in this case, Na_2CO_3. Max. efficiency and min. steam requirements with the same temp. parameters are given. Similar data for methylamine sulfite solutions are given in Fig. 3. The use of Na or methylamine sulfite soln. for recovery of SO_2 requires larger quantity of steam for regeneration than the use of ammonium sulfite soln. but the Na or methylamine sulfite soln. permits the use of high temperatures for regeneration, thereby obtaining a more complete desorption of SO_2.

68. Kopita, R., & Gleason, T.G. (Peabody Eng. Corp. N.Y., N.Y.) Wet scrubbing of boiler flue gas. Chem. Eng-Prog. 64, Jan. 1968, p. 74-78.

A wet scrubbing system can be designed to remove 99+% of the fly ash from the stack gas and also 70-99.5% of the SO_2 in the same gas (70% by using plain water and 99.5% by using aq. Na_2CO_3). Such a system would be economical to use, compared to the alternative of using extra-low-S fuel.

69. Sakol, S.L. & Shah, I.S. (Chemical Construction Corp.) Removal of sulfur dioxide from clay kiln exhaust gases. Chemico Brochure, 1968, 10 pp.

In the ceramic industry, the waste gases from the kilns contain an appreciable amount of SO_2. To eliminate air pollution due to this SO_2, Chemico has developed a scrubbing system using as absorbent an aq. solution of NaOH or Na_2CO_3 or a slurry of quick lime (5%) in a Venturi scrubber. For a capacity of 10,000 SCF/min., waste gas, the equipment cost is estimated at $47,000, and operating cost $14,250 per yr.

70. Skrivanek, J., & Cada, V. Absorption of sulfur dioxide in a Venturi tube. Chem-Prumysl 7, 340-3 (1957); C.A. 52, 14993 i (1958).

Absorption of sulfur dioxide in a Venturi tube. Expts. with absorption of a gas contg. 0.2% SO_2 in Na_2CO_3 solu. in a Venturi tube were arranged in a factorial manner based on statistical methods, and the degree of absorption and the pressure drop were followed. An equiation is presented correlating the processing conditions. The efficiency of absorption increased with the velocity of the gas. At the optimum conditions an absorption of 68% at a pressure drop 610 mm. H_2O is reported.

71. Trendafelov, D., Ponyankov, B., & Zapryanova, A. Extraction of sulfur dioxide from smoke gases. Khim. Ind. (Sofia) 35 (1), 3-5 (1963); C.A. 59, 6892 e (1963).

Absorption of SO_2 by aq. Na_2CO_3 in a recovery system can be complete at 50°.

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72. Nakazono, T. (to Furukawa Kogyo K.K.) Recovering sulfur dioxide. Jap. Pat. 172,814, May 31, 1946; C.A. 43, 7201 f (1949).

An aq. soln. of an alkaline earth or alkali salt of HCOOH is used as the absorbent for SO_2. The SO_2 is recovered by heating the aq. soln. The latter is then recycled to the absorber.

73. Anon. -1969, Chemico looks at sulfur recovery. Europ. Chem. News 15, Feb. 28, 1969, p. 26.

The various processes for the removal and recovery of SO_2 from waste gases are briefly described and their economics are discussed. Among several proprietory processes mentioned is the one used by Stone and Webster Co. which uses caustic soda to absorb SO_2 resulting $NaHSO_3$ in the pregnant solution. The SO_2 is then stripped from the solution and recovered.

74. Anon. -1969. Kureha Chemical create desulfurization technique. Japan Chem. Wk. 10, Jan. 23, 1969, p. 1; Chem. Eng. 76, Feb. 10, 1969, p. 38.

Under construction is a desulfurization unit at Kureha's power generating plant at Nishki, Fukushima Prof. capable of treating 330,000 cu. m. gas per h. producing 18,000 tons Na_2SO_3 per yr. consuming 680 Kg NaOH per ton of Na_2SO_3 reocvered. Removal efficiency is 95%.

75. Franz, M., & Klimecek, R. Processing sulfur dioxide from combustion gases. Czech. Pat. 110 995 May 15, 1964 (Appl. July 22, 1961); C.A. 61, 14233 d (1964).

The SO_2 is absorbed in aq. NaOH. The pregnant soln. is acidified with H_2SO_4 to pH of about 1.0 to liberate SO_2. The resulting Na_2SO_4 soln. is partly electrolyzed to recover NaOH and H_2SO_4 separately. The NaOH and H_2SO_4 are recycled, resp.

76. Germerdonk, R. (Farbenfabriken Bayer AG, Lieverkusen, Germany). Scrubbing sulfur dioxide from the gases. Chem. -Inq. -Tech. 37, 1136-9 (Nov. 1965).

Data on scrubbing with NaOH solution are given.

77. Spalding, C.W., & Han, S.T. (Inst. of Paper Chem., Appleton, Wis.) Absorption with chemical reaction from a dilute gas in packed towers. Tappi 45 (3) 192-9 (1962); C.A. 60, 12906 h (1964).

The design procedure and operating characteristics of packed columns are discussed using water and NaOH soln., resp., as absorbents.

78. Takeuchi, N., & Namba, Y. (Univ. Hiroshima, Japan). Absorption of sulfur dioxide. Hiroshima Daigaku Kogokubu Kenkyu Hokoku 12 (2), 241-250 (1964); C.A. 61, 15395 e (1964).

The rate of absorption of SO_2 in aq. NaOH was measured. The data were in agreement with the theoretical valued corresponding to the instantaneous, 2nd-order irreversible chem. reaction.

79. Rozie, M. and Desire, P. (to Societe Progil, Paris, France). Process for recovery and use of sulfur dioxide. U.S. Pat. 3 431 072 (Cl. 23-165) March 4, 1969 (appl. March 27, 1961).

A scrubbing solution is prepared by neutralizing H_3PO_4 with Na carbonate. The tail gas from the H_2SO_4 plant containing residual SO_2 (about 0.2%) is scrubbed with the Na phosphate solution which reduces the SO_2 content to about 40 ppm. $NaHSO_3$ and NaH_2PO_4 are formed in the solution which is withdrawn from the bottom of the scrubbing column and pumped to the top of the stripping column where 92% H_2SO_4 is sprayed and mixed with the SO_2-rich solution. Air is blown into the stripping column at its bottom. The air carries the SO_2 liberated by H_2SO_4 out of the column at its top. This air then contains a controlled amount of SO_2 suitable for use as feed gas to the H_2SO_4 plant. The liquid effluent from the stripping column containing H_2SO_4, NaH_2PO_4 and some Na_2SO_4 is sent to the H_3PO_4 plant as part of the acidulating agent for the pulverized phosphate ore.

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80. Cederquest, K.N., Ahlborg, N.K.C., Lunden, B., & Wentworth, T.O. Stora sodium-base chemical recovery process. Tappi 43, 702-6 (Aug. 1960).

The chemicals recovery system of Stora Kopparbergs Bergslags, A. B., Sweden is described with flow diagram. Briefly the sulfite plup mill and the sulfate craft mill are integrated. The Na_2S0_4 in the waste liquor is smelted to give $C0_2$ and H_2S. The H_2S is converted to S by the Claus process. The S together with make-up S is burnt to give $S0_2$. The burner gas is water-scrubbed to give a 2% aq. $S0_2$ soln.; the latter is heated to give a 90% $S0_2$, 10% H_20 gas. The residual $S0_2$ in the tail gas from the water scrubber is absorbed in aq. Na_2S0_3 soln. The latter soln. leaving the $S0_2$ absorption tower contains 70 g/l Na_20 and $S0_2$. This solution is used to convert Na_2C0_3 and $NaHC0_3$ obtained from the smelting step into Na_2S0_3. The latter is adjusted to the proper pH value and sent to the wood-chip digester. A part of this Na_2S0_3 soln. is recycled to the $S0_2$ absorber.

81. Johnstone, H.F., Read, H.J., & Blankmeyer, H.C. (Univ. of Ill., Urbana). Recovery of sulfur dioxide from waste gases. Equilibrium vapor pressures over sulfite-bisulfite solutions. Ind. Eng. Chem. 30, 101-109, (1938).

Figure 2 shows the capacity of Na_2SO_3-$NaHSO_3$ solutions for recovery of SO_2 from gases contg. 0.3% SO_2 at absorption temps. of 35°, 45° and 55°, resp., and desorption temps. of 70°, 80°, 90°, 100°, and 120°. The capacity is defined as the difference between SO_2 concn. in solution leaving absorber and that leaving the regenerator for a constant concn. of a base, in this case, Na. Max. efficiency and min. steam requirement with the same temp. parameters are given. Similar data for methylamine sulfite solutions are given in Fig. 3. The use of Na or methylamine sulfite soln. for recovery of SO_2 requires larger quantity of steam for regeneration than the use of ammonium sulfite soln. but the Na or methylamine sulfite soln. permits the use of high temps. for regeneration, thereby obtaining a more complete desorption of SO_2.

82. Johnstone, H.F. & Singh, A.D. (to Commonwealth Edison Co., Chicago, Ill.) Process for recovering sulfur dioxide from waste gases. U.S. Pat. 2 161 056 (Cl. 23-178) June 6, 1939 (appll Mar. 24, 1937). C.A. 33, 7500 (6) (1939).

Apparatus and process for recovering SO_2 from dil. gases which consists in absorbing the SO_2 in an aq. soln. of Na_2SO_3 and $NaHSO_3$, treating the enriched soln. with ZnO, removing pptd. $ZnSO_3$ from the soln., returning the soln. to contact with the gases in a cyclic manner, drying the Zn sulfite and heating it to decompn. into ZnO and SO_2, collecting the SO_2, and returning the ZnO for further treatment of the enriched soln.

83. Johnstone, H.F., & Singh, A.D. (Univ. of Illinois, Urbana). The recovery of sulfur dioxide from dilute waste gases by chemical regeneration of the absorbent. Univ. of Illinois Eng. Expt. Station Bul. Ser. No. 324; Univ. of Illinois Bul 38, No. 19, Dec. 31, 1940, 137 pp; C.A. 35, 2301 (9) (1941); cf U.S. Pat 2 161 056 (1939).

A commercially workable process for the recovery of SO_2 from waste gases is described. The waste gases are scrubbed with an aq. soln. of Na_2SO_3 and NaH_2SO_3. The fouled soln. is regenerated by the addn. of ZnO which ppts. $ZnSO_3 2.5H_2O$ in a well-defined cryst. form which settles rapidly. The $ZnSO_3$ is dewatered and calcined to liberate the SO_2. When dealing with gases contg. 0.3% SO_2, the oxidation is approx. 10% of the SO_2 absorbed. The SO_4 formed is removed by means of lime. The cost of the equipment for a plant treating 100,000 cu. ft. of gas per min. at 300°F. contg. 0.3% SO_2 and recovering 21.7 tons of SO_2 per day would be approx. $140,000. This includes machinery for the liquefaction of the SO_2. The fixed charges and operating costs are approx. $15.40 per ton of SO_2. The advantages of this process are - (1) The clear, neutral liquid gives a high rate of absorption and freedom from severe corrosion difficulties. (2) The pptn. of the scale-forming salts outside of the scrubber permits the use of cycline spray scrubbers without danger of clogging of the nozzles. (3) There is no danger of loss of chemical by volatilization. (4) Pure SO_2 is produced. A detailed study of each step in the process and a flow sheet is given.

84. Johnstone, H.F., and Singh, A.D. Recovery of sulfur dioxide from waste gases. Ind. Eng. Chem. 32, 1037-1049 (1940).

A new process for the regeneration of sulfite-bisulfite solutions used for absorbing sulfur dioxide from waste gases is described. It is based on the precipitation of zinc sulfite, followed by decomposition of the dried solid in a flash calciner to give pure sulfur dioxide and zinc oxide, the latter being recycled. A thorough study in the laboratory and pilot plant has given important information on several of the unit operations. The paper includes a discussion of the design of flash calciners based on the transfer of heat to particles suspended in gas streams. Data are presented on the rate of oxidation of sulfite-bisulfite solutions in the recovery process from actual plant operation, and a new flow sheet for desulfation is described.

85. Lynn, S., Straatemeier, J.R., & Kramers, H. (Tech. Hogeschool, Delft, Netherlands). Absorption studies in the light of the penetration theory. I. Long wetted-wall column. Chem. Eng. Sci. 4, 49-57 (Apr. 1955); C.A. 49, 10671 f (1955).

    The absorption of SO_2 by aq. $NaHSO_3$ soln. of concns. of 0.196 and 1.087 N, resp., was investigated. The diffusivity of SO_2 in the soln. at 20° was found to be 1.40 and 1.25 times 10^{-5} cm^2/sec, resp. The presence of surface-active agent in the soln. was found to have no effect upon the rate of absorption (g./cm^2./sec.) into the liquid film, which is a function of diffusivity. Under similar conditions the diffusivity of SO_2 into pure water and found as 1.46 x $10,^{-5}$ indicating the mass effect of HSO_3 upon absorption of SO_2 in water.

86. Monev, G., Tartarski, A., & Kircheva, N. Purification of flue gases from sulfur dioxide. Godishnik Nauchnoizsled. Inst. Khim Prom. 2, 5-20 (1963) (in Gulgarian); C.A. 62 7407 f (1965).

    The SO_2 contg. gas is scrubbed with aq. Na_2SO_3 soln. The pregnant solution contg. $NaHSO_3$ is treated with MgO according to the equation $2NaHSO_3 + Mg0 + 5H_2O \rightarrow Na_2SO_3 + MgSO_3.6H_20$. The $MgSO_3.6H_20$ is separated by crystallization and centrifuging. The mother liquor contg. Na_2SO_3 is recycled to the scrubber. The $MgSO_3.6H_20$ is dired and calcined to liberate SO_2 and regenerate MgO. The SO_2 is suitable for making H_2SO_4.

87. Wang, J.C., & Himmelblau, D.M. (Univ. of Texas, Austin). A kinetic study of sulfur dioxide in aqueous solution with radio-active tracers. A.I.Ch.E. Journal 10 (4), 574-580 (1964); C.A. 61, 8939 g (1964).

    In an aq. soln. of Na_2SO_3 the reaction rate constants for forward and backward directions in $SO_2 + H_2O \rightleftharpoons H^+ + SHO^-3$ were determined with the aid of radio-active tracer S-35. Data cover temps 0°-20°, and pH 1.25-4.3.

88. Whitney, R.P., et al. On the mechanism of sulphur dioxide absorption in aqueous media. Tappi 36, No. 4, April 1953, pp. 172-175; C.A. 47, 11727 b (1953).

    SO_2 absorption by aq. Na_2SO_3 soln. was studies using a 4 inch diam., 24-inch high column of 1-inch Rasching rings. The rate of absorption was measured at 100°F. and a liquid rate of 3130 lb/(h) (sq.ft. of column cross-section). The liquor contained 1.0M Na_2SO_3. Various values of SO_2 partial pressures were used. A curve was plotted with K_Ga vs. G. (K_Ga = overall coefficient in lb. males of SO_2 per (h.) (cu.ft.) (atm.); and G = average overall total gas rate at top and bottom of column.)

89. Anon. -1968. Some details of the Beckwell process for removing sulfur dioxide. Chem. Week 103, July 27, 1968, p. 57; cf Belg. Pat. 706-449 (1968).

The Beckwell process is jointly developed by Bechtel Corp. and Wellman-Lord Eng., Inc. and is based on the absorption of SO_2 from flue gases and H_2SO_4 plant tail gases by hot K_2SO_3 solution. The pregnant solution containing $KHSO_3$ and very little K_2SO_3. A portion of the pregnant solution is cooled to crystallize K pyrosulfite. The crystals are separated and heated to convert them to K_2SO_3 with liberation of SO_2 which is recovered as a pure gas. The K_2SO_3 is recycled.

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90. Keller, J.L. (to Union Oil Co.) Removal of sulfur dioxide from gases containing the same. U.S. Pat 2 729 543, Jan. 3, 1956.

The SO_2 in a gas is absorbed in a solution of Na thiosulfate, buffed to give a pH value of 4-6. The solution after use is regenerated by contacting H_2S gas at 40°-100° so that elemental S is formed. After removal of S by filtration the thiosulfate solution is recycled. In the regenerating step, the solution is taken out of contact with H_2S gas as soon as the stoichiometric amount of H_2S has dissolved in the solution.

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91. Bevans, R.S., Renzi, P.N., and Loonkar, Y.R. (to American Standard Inc.) Method of removing sulfur compounds and recovering heat from combustion gases. U.S. Pat. 3 386 798 (Cl. 23-2) June 4, 1968 (appl. Nov. 30, 1964).

The scrubbing solution is essentially a soln. of $CaCl_2$ and $Ca(OH)_2$. In order to use it to remove SO_2 from the hot flue gas from thermal power plants a concentrated (e.g. 35-45%) $CaCl_2$ soln. has the advantage of lower vapor pressure and therefore it can be operated at a higher temp. The $CaSO_3$ thus formed has low solubility; therefore it may be removed as a solid precipitate by settling or filtration. After circulating through the hot SO_2 scrubber, some of the heat content in the scrubbing soln. may be recovered by heat exchange with the air going into the combustion chamber.

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92. Furufugi, I. (to Toa Gosei K.K.) Treatment of sulfur dioxide in flue gas. Jpa. Pat. 174 880 June 6, 1948; C.A. 43, 7201 g (1949).

SO_2 in flue gas is adsorbed on C particles suspended in water. Example: a gas contg. 0.7% SO_2 was scrubbed with a liquid contg. 600 liters of c dust in 135 cu. m. of water; the effluent gas contained 0.04% SO_2.

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93. Barwasser, J., & Roesner, G. (Lurgi-Gesellschaft, Chemie Huttenqesen m. b. H.) Obtaining sulfur dioxide from industrial gases. Reichsamt Wirtschaftsausbau. Chem. Ber. Pruff-Nr. 93, (PB 52008), 135-48 (1940) (Pub. 1941); C.A. 41, 6374 i (1947).

Processes using H_20, basic $Al_2(S0_4)_3$ soln., $(NH_4)_2SO_3$ soln. as absorbent are discussed. The "Sulfidin" process is specially mentioned. It uses a 1:1 or 1:2 mixt. of xylene and H_20 as the absorbent, economy of this process is claimed. Absorption isotherms are given for $S0_2$ in H_20, basic $Al_2(S0_4)_3$ soln and xylene.

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94. Bergars, D. J. (to Imp. Chem. Inds. Ltd.) Treatment of gases with liquids. Brit. Pat. 680 868 Oct. 15, 1953; C.A. 47, 4664 f (1953).

Flue gases from coal or oil-fired furnaces have been treated with a slurry of $Ca(0H)_2$ in a tower packed with layers of bars. The efficiency of $S0_2$ removal was 96%.

95. Lessing, R. (to Imp. Chem. Inds. Ltd.) Purifying combustion gases containing oxides of sulfur. U.S. Pat 2 080 779 May 18, 1937; C.A. 31, 5138 (9) (1937).

Aq. $CaCO_3$ slurry is used as $S0_2$ absorbent.

96. Nakagawa, S. Removal and utilization of sulfur dioxide in stack gas by the JECCO process. Ryuson 16, 211-8 (1963); C.A. 60, 10251 c (1964). (cf. ref. 213).

The JECCO process uses either $(NH_4)_2S0_3$ or milk of lime as the absorbent for $S0_2$, and recovers $(NH_4)_2S0_4$ or gypsum, resp., as product.

97. Nonhebel, G. et al. (to Imp. Chem. Inds. Ltd.) Purifying gases from the combustion of sulfur contg. fuels. U.S. Pat 2 090 142 Aug. 17, 1937; C.A. 31, 7231 (5) (1937).

The gases contg. S oxides is scrubbed with an aq. soln. contg. milk of lime. The operation yield $CaS0_3$ and $CaS0_4$ which ppt. from the scrubbing soln. The pptd. $CaS0_3$ and $CaS0_4$ ppts. are removed from the scrubbing soln. fresh milk of lime is added and the reinforced soln. is recycled.

98. Shneerson, B.L. et al. Removal of sulfur dioxide from flue gases. Russ. Pat. 50 446 Feb. 28, 1937; C.A. 31, 8894 (7) (1937).

About 50% of the $S0_2$ is oxidized to $S0_3$, the rest is absorbed in aq. $Ca(OH)_2$. The $CaS0_3$ soln. thus formed is treated with H_2S0_4 formed by oxidation to separate $S0_2$ from $CaS0_4$.

99. Tennessee Valley Authority. Sulfur dioxide removal from power plant stack gas: use of limestone in wet scrubbing. National Air Pollution Control Admin. Report, 1969, 104 pp.; PB 183 908, clearinghouse, Springfield, Va., $3.00

Powdered limestone (or dolomite) may be injected into the fire box of a power plant boiler, or may be fed into the water in a scrubbing system. Each of these methods has advantages and disadvantages; but the most important considerations are that the injection method is simpler and less costly to operate, and that the slurry scrubbing method removes SO_2 more completely (>90% vs. 50-60%). The limestone injection with no subsequent scrubbing but with a dry dust removal system does not appreciably lower the stack gas temp. On the other hand, any wet scrubbing would reduce stack gas temp. to the saturation temp. (about 125°F) and would require reheating of the flue gas to prevent visible vapor trail from the stack and to prevent great reduction of plume rise for good dispersion. Neither dry limestone injection method nor limestone slurry scrubbing method recovers the S values in the stack gases, and both methods have a solid waste disposal problem. The scrubbing water can be recycled after settling out the solids which are mostly $CaSO_4$ and $CaSO_3$. Lime may be used instead of limestone in the slurry scrubbing method. The use of lime would require a lower liquid rate in the scrubber, but lime is more expensive and the overall cost of operation is in favor of limestone. Capital and operating costs for an installation of a limestone slurry scrubbing unit attached a 200 Mw power plant are estimated in detail. Plant layout and equipment specifications are given.

100. Wilton, T. O., Wilton, N., Green, H. E. J., & Mann, H. C. Washing and purifying flue gases. U.S. Pat 2 073 039 Mar. 9, 1937; C.A. 31, 3244 (7) (1937).

SO_2 and SO_3 in the flue gas are removed in 2 stages. In the 1st stage the gases are scrubbed with milk of lime of such concn. as to form only Ca bisulfate and bisulfite. In the 2nd stage, the liquor from the first stage is treated with more milk of lime to ppt. the normal Ca sulfite and Ca sulfate which are removed by settling and filtration.

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101. Babushkina, M. D., Babaev, E. V., & Molchanova, N. I. Preparation of magnesium-base cooking liquors. Bumazhn. Prom. 38, (5), 7-10 (1963); C.A. 59, 7746 f (1963).

Considering the increasing use of the Mg-base sulfite pulping process, a study was made of the mechanism of SO_2 absorption by aq. suspensions of MgO, and specifically, of the effect of suspension concn. and of reaction time on the formation of sulfite-bisulfite solns. The concn. of the gaseous SO_2 to be absorbed was kept const. at 11-12%. The MgO suspensions were prepd. in concns. of 1, 3, and 10% from caustic magnesite (a waste product of the conversion of magnesite into metallurgical powders), contg. 83-86% MgO and an amt. of impurities within the limits of the standard specifications. The reaction was carried out to a total concn. of SO_2 in the system of 2.5-5%. The total SO_2 concn. was detd. only by the reaction time and did not depend on the concn. of the MgO suspension. The distribution of bound SO_2 between the liquid and the solid phase, and the concn. of bound SO_2 in soln. depended on the concn. of the suspension. In 1% suspensions, absorption of SO_2 resulted in the accumulationof bound SO_2 mainly in the liquid phase and the SO_2 accumulated at a uniform rate. In 10% suspensions, the bulk of the bound SO_2 was found in the solid phase, and its accumulation curve showed a max. The reactions in the 3% MgO suspension had a character intermediary between those occurring in the 1% and the 10% suspensions. At first, only $MgSO_3$ was found in soln., then, with crystn. of $MgSO_3$, and hence with accumulation of SO_2 in the solid phase, $MgSO_3$ and $Mg(HSO_3)_2$ were both found in soln. At the same time, the concn. of bound SO_2 in the solid phase began to decrease. In the 1st phase, up to the crystn. of sulfite, the reaction was similar to that in 10% suspension, and the 2nd phase corresponded to the reaction occurring in the 1% suspension. Evidently, in dil. MgO suspensions, the decompn. of $Mg(HSO_3)_2$ by excess MgO is insignificant and no supersatn. with $MgSO_3$ takes place, while this reaction predominates in concd. suspensions.

102. Chertkov, B. A. Mass-transfer coefficients in the absorption of sulfur dioxide from gases by magnesium sulfite-bisulfite solutions. Khim. Prom. 1963 (7), 537-541; C.A. 60 2558 f (1964).

The absorption of $S0_2$ from industrial waste gases, contg. 0.25-0.35% $S0_2$ by wt., at 150-70° was studied with an absorber irrigated with a Mg sulfite-bisulfite soln. contg. suspended $MgS0_3 \cdot 6H_20$ crystals and some impurities, at pH 5.1-6.2. The resistance to mass transfer in the liquid phase was insignificant, and the overall mass-transfer coeff. was practically equal to the gas-phase mass-transfer coeef. The relation between the Nusselt and Reynolds nos. obeyed the equation $Nu_g = 0.0035\, Re_g Re_l^{0.4}$ (subscripts g and l designate the gas and liquid phases., resp.) The resistance to mass transfer in the liquid phase increased with decreasing pH, probably because of the increased relative concn. of Mg bisulfite.

103. LaBerge, J.C. (Weyerhaeuer Co., Longview, Wash.) Sulfite Mg0 system-$S0_2$ absorption efficiency improvement. Tappi 46, (9) 538-41 (1963); C.A. 59, 11005 h (1963).

$S0_2$-contg. boiler flue gases and vent gases enter cooling towers, the $S0_2$ burner gas is mixed with the digester gas, and both pass into a tower used for fortification of the product acid from the absorption trains. The overhead gas from this tower is mixed with cooled flue gas. $S0_2$ is absorbed in spray towers with concurrent flow and the remaining $S0_2$ passed into 3 towers with counter current flow. These are packed with partition rings. The gases are force-drawn through the towers by draft fans.

104. Lowenstein-Lom, W.G. (to Standard Oil Dev. Co.) Removal of sulfur oxides from flue gases and their conversion to ammonium sulfate. Brit. Pat. 708 095, Apr. 28, 1954; C.A. 48, 11033 c (1954).

Gases contg. $S0_2$ and $S0_3$ are scrubbed with an aq. suspension of $Mg(0H)_2$. The spent scrubbing soln. now contg. $MgSO_3$ and $MgS0_4$ is aerated and oxidize $MgS0_3$ into $MgS0_4$. After this operation the solution is treated with NH_3 gas to convert $MgS0_4$ into $Mg(0H)_2$ and $(NH_4)_2S0_4$. The $Mg(OH)_2$ separated and used to make a fresh suspension for scrubbing. The $(NH_4)_2S0_4$ soln. is concentrated to crystallize the $(NH_4)_2S0_4$.

105. Pinaev, V.A. Removal of sulfur dioxide from gases from agglomerating plants by a method using crystalline magnesite. Vestn. Tekhn. i Ekon. Inform. Nauchn.-Issled. Gas. Kom. Sov. Min. SSR po Khim 1962 (5) 51-56; C.A. 59, 13621 d (1963).

$S0_2$ in the waste gases from the sintering plant may be recovered by scrubbing the gas with slurry of Mg0. The Mg0 is thereby converted to $MgS0_3$ which ppts. out as $MgS0_3 \cdot 6H_20$. The latter is calcined at 850°-900° to drive out $S0_2$ and regenerate Mg0.

106. Potop, P., Creanga, L., & Theodorescu, C. Recovery of sulfur dioxide from residual gases by wet absorption in two purification steps. Rev. Chim. (Bucharest) 17 (6), 331-6 (1966); C.A. 65, 14896 e (1966).

The gas to be treated contained 0.1 to 0.7% $S0_2$. The $S0_2$ was recovered in 2 steps. The first step was scrubbing the gas with a spray of $Mg0$ or $Mn0$ slurry in water. The resulting gas contained 0.01% $S0_2$. The $Mg0$ or $Mn0$ became $MgS0_4$ or $MnS0_4$, resp., which was calcined to give $Mg0$ and Mn_20_3, resp., and a gas contg. 5-8% $S0_2$ which could be used to make H_2S0_4. The second step was to take the effluent gas from the 1st-step scrubber contg. 0.01% $S0_2$ and pass it through a column packed with active C and sprayed with a soln. of $(NH_4)_2S0_3$ contg. free NH_3 (the NH_3 fed into the system is approx. equivalent to the $S0_2$ in the gas). The effluent of the 2nd-step scrubber contained 0.001-0.002% $S0_2$. $(NH_4)_2S0_4$ was recovered from the scrubbing liquor by concentration (evaporation) and crystallization. The mother liquor separated from the crystals was reinforced with NH_3 and recycled to the scrubber.

107. Ruhrchemie AG. Eliminating sulfur dioxide in gases. Belg. Pat. 628 092, Aug. 6, 1963 (Ger. Appl. March 13, 1962); C.A. 60, 11656 b (1964).

Gases contg. a low concn. of $S0_2$ are scrubbed with an aq. slurry of $Mg0$, $Mg(0H)_2$, $MgC0_3$ or $Mg(HC0_3)_2$. The $S0_2$ is oxidized to $S0_3$ during absorption so that $MgS0_4$ is formed. $Mg(0H)_2$ is regenerated by adding NH_3 to ppt. $Mg(0H)_2$. After filtering off $Mg(0H)_2$ the $(NH_4)_2S0_4$ is recovered from the mother liquor.

108. Zalogin, N. H_2S0_4 from the smoke of electric power stations. Novosti Tekhniki 1940, No. 21-22, p. 46-48; C.A. 37, 6413 (6) (1943).

The flue gas contg. 0.35% $S0_2$ is scrubbed with a water slurry of $Mg0$. The $S0_2$ combines with $Mg0$ to form soluble $MgS0_4$ and solid $MgS0_3 \cdot 6H_20$ The latter is collected and calcined at 900° to recover $S0_2$ and $Mg0$. The $Mg0$ is recycled. The $MgS0_4$ is also recovered as a by-product.

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109. Anon.-1966. H_2S0_4 and Cl_2 from waste gas. Europ. Chem. News 10, Oct. 28, 1966, p. 46; cf. Brit. Pat. 1 041 822 (to Mitsubishi Shipbuilding and Engineering Co., Ltd., Japan.)

Gases contg. $S0_2$ is scrubbed with a 30% slurry of Mn oxide to absorb $S0_2$ forming $MnS0_4$. The slurry containing $MnS0_4$ is treated with HCl to form $MnCl_2$ and H_2S0_4. The $MnCl_2$ is crystallized out of the aqueous soln. as $MnCl_2 \cdot 4H_20$. It is dried, dehydrated and 200° and calcined at 500°-900° to convert it to $Mn0$ and Cl_2 gas. The $Mn0$ is reused. The H_2S0_4 produced earlier in the process is used with NaCl to produce HCl.

110. Andrianov, A. P. Combined method of purification of flue gases from oxides of sulfur. Novost: Tekhniki 1936, No. 58-59 14-16; C.A. 31, 3666 (9) (1937).

The gases contg. $S0_2$ is first treated with an aq. slurry of $Mn0_2$ and $FeS0_4$ so that 50% of the $S0_2$ is removed. The gases are then scrubbed with milk of lime. The first treatment yields H_2S0_4 and the 2nd treatment yields $CaS0_3 \cdot 2H_20$. Combining the two and heating to 90° yields a gas contg. 90-95% $S0_2$.

111. Atsukawa, M., Matsumoto, K., & Murokawa, H. (to Mitsubishi Shipbuilding & Engineering Co., Ltd., Tokyo). Process of treating waste gas containing sulfur oxide. U.S. Pat 3 226 192 (Cl. 23-167). Dec. 28, 1965. (Japan appl. Feb. 28, 1962).; Brit. Pat. 1 041 822, Sept. 7, 1966.

Waste gases containing SO_2 is scrubbed with a thick Mn-oxides slurry. Thus the spent slurry contains Mn sulfate. The spent slurry is regenerated in the liquid form with HCl so as to form $MnCl_2$ and H_2SO_4. The $MnCl_2$ is crystallized and separated. It is then treated with hot combustion gas with excess O_2 to convert the $MnCl_2$ into Cl_2 gas and Mn oxides which are re-slurried and reused.

112. Mitsubishi Shipbuilding & Eng. Co. Ltd. Sulfur oxides removal from stack gases and sulfuric acid manufacture. Fr. Pat. 1 348 923-4 (Cl. C 10b, 10k, F 23j) Jan. 10, 1964 (Japan. ppl. Feb. 28, 1962); C.A. 61, 6657 e, f (1964).

Stack gas contg. 0.17% $S0_2$ and 2.8% 0_2 is scrubbed with a slurry of 8% Mn0 in water at 45°-50°. The gas is thus freed from $S0_2$. The pregnant soln., aside from the suspended solids, contains $MnS0_4$ 24.3% MnS_20_6 0.9% and H_2S0_4 0.8%. The $MnS0_4$ is crystallized as $MnS0_4 \cdot 4H_20$. The latter is converted to $MnCl_2 \cdot 4H_20$ with HCl or NaCl. The $MnCl_2 \cdot 4H_20$ is oxidized at 350° - 600° to regenerate Mn0 and HCl.

113. Peisakhov, I. L. Catalytic purification of flue gases from sulfur dioxide. Novosti Tekhniki 1936, No. 58-59, 13-14; C.A. 31, 3666 (7) (1937).

$S0_2$ in gases is removed by washing the gases with a soln. contg. dissolved or suspended $Mn0_2$ or a mixt. of $Mn0_2$ and $FeS0_4$. The reaction between $S0_2$ and the said soln. yields H_2S0_4. The mixture of $Mn0_2$ and $FeS0_4$ as catalyst for the oxidation of $S0_2$ is very stable and gives a 14-15% H_2S0_4.

114. Tarbutton, G., Jones, T. M., & Driskell, J. C., & Smith, C. M. (to TVA) (Muscle Shoals, Ala.) Manganese oxide process for the recovery of sulfur dioxide from waste gases. U.S. Pat. 2 984 545 (Cl. 23-178) May 16, 1961 (Appl. Feb. 27, 1958).

Waste gases containing SO_2 is scrubbed with a water slurry of Mn oxides. The SO_2 combines with the Mn oxide to form a sulfite in the form of a precipitate. The Mn sulfate is filtered out and dried and calcined to drive SO_2 out and thus regenerating the Mn oxides. The hot Mn oxide is exposed to air to alter its state of oxidation so that the absorptive power of the slurry made from it is improved.

115. Tarbutton, G., Driskell, J. C., Jones, T. M., Gray, F. J., & Smith, C. M. (TVA, Wilson Dam, Ala.) Recovery of sulfur dioxide from flue gases. Ind. Eng. Chem. 49, 392-5 (1957).

Four processes for recovering SO_2 from flue gas have been invetigated, all using Mn oxides, suspended in an aq. soln., as catalyst: (1) direct absorption of SO_2 in the presence of O_2; (2) absorption of SO_2 in aq. soln. followed by aeration of the soln. with air contg. O_3; (3) absorption of SO_2 from gas contg. O_3 in a slurry of MnO_2 contg. NH_3; and (4) scrubbing the SO_2-contg. gas with a 10% slurry of Mn oxides obtained from calcining $MnSO_4$ at 1000°-1100° without added ozone. The last mentioned process appears most promising. In a pilot plant test a gas contg. SO_2 0.26; O_2 2.4; CO_2 15.6; and N_2 81.7% is scrubbed with a 10% Mn oxide slurry at 60° for a contact time of 7.5 sec.; essentially all of the SO_2 was absorbed. At the end of 72 hours of continuous operation the slurry was filtered and the filtrate contained an equivalent of 29% anhy. $MnSO_4$. About 10.5% of the Mn in soln. was in the form of dithionate only a trace of H_2SO_4 was present. 28 references.

116. Vasil'ev. S.S., Kashtanov, L.I., Kastorskaya, T. L. & Nemkova, O. G. Application of catalysts and ozone in the water purification of flue gases from sulfur dioxide. Novosti Tekhniki 1936, No.58-59, p. 12-13; C.A. 31, 3666 (5) (1937).

A soln. of Mn salts (0.1%) used for the absorption of SO_2 results in a 25% H_2SO_4 soln. The action of O_3 in the process of SO_2 oxidation depends on the ratio of O_3 concn. At equal concn. one mole of H_2SO_4 is formed per mole of O_3; if there is a high excess of SO_2, then 15-20 moles of H_2SO_4 is formed per mole of O_3. This is explained by the chain reaction between O_3 and SO_3. There is probably a catalyst formed in the soln.

117. Zimmerley, S.R. (to Kennecott Copper Corp.) Use of deep-sea nodules for removing sulfur compounds from gases. U.S. Pat. 3 330 096 (Cl. 55-73) July 11, 1967 (Appl. Feb. 19, 1965).

Deep-sea Mn nodules are found to absorb SO_2 to the extent of 25% of their own weight. They are specified to be used in a loose packed bed to remove SO_2 from waste gases.

118. Atsukawa, M., Nishimoto, Y., & Matsumoto, K. (Hiroshima Tech. Inst. Japan). Removal of SO_2 gas from waste gases. Mitsubishi Heavy Inds. Ltd., Tech. Rev. 2, No. 2, 51-57 (May 1965).

The processes for the removal of SO_2 from flue gas are reviewed. Tests are being completed by Mitsubishi Heavy Inds. Ltd. on a new process using a slurry of red mud from the bauxite processing, as the SO_2 absorbent.

119. Fukuma, S., Atsukawa, M., & Inoue, Y. (To Mitsubishi Shipbuilding & Engineering Co. Ltd., Tokyo). Production of sulfites from red mud. U.S. Pat. 3 298 781 (Cl. 23-121) Jan. 17, 1967. (Japan, appl. Feb. 9, 1962).

SO_2 in waste gases is removed scrubbing with a slurry contg. up to 40% red mud (the residue of treating bauxite with an alkaline soln. in the Bayer process). The slurry may be used at 20°-70°C. until its pH value drops to 4.3. Upon filtration an aq. soln. of Na_2SO_3 and $NaHSO_3$ may be recovered.

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120. Hrdlicka, K. Absorbing sulfur dioxide and trioxide from industrial fumes by the zinc method. Czech Pat. *90 701, June 15, 1959; cf.* Tech. Chem. (Prague) 12 (5), 236-241 (1962); C.A. 54 9230 d (1960); 61, 3608 e (1964).

The SO_2 contg. gas is scrubbed with a slurry of ZnO producing $ZnS0_3 . 2.5H_20$ crystal. Two methods of liberation of $S0_2$ and regeneration of Zn oxide are available: one is thermal decomposition, and the other is treating the $ZnS0_3$ in soln. with H_2S0_4. However the second method does not regenerate Zn0, but gives a byproduct of $ZnS0_4$, which is not always economical unless suitable Zn0 in large supply is available.

121. Klimecek, R., & Jara, V. Absorbing sulfur dioxide from industrail waste gases. Czech. Pat. 106 829, Mar. 15, 1963 (appl. Nov. 26, 1961); C.A. 60, 3915 b (1964).

The presence of 0.5-50 g./l. of Na0H, K0H, or NH_40H in the Zn0 slurry increases the efficiency of scrubbing from 70-80% to 80-90% at the same liquid rate.

122. Metallgese lschaft AG. (Bakay, T., inventor). The decomposition of $ZnS0_3$ obtained from the purification of fume gas which contains sulfur dioxide. Fr. Pat. 1 370 520 (cl. C 016) Aug 21, 1964 (Ger. appl. Dec. 12, 1962); C.A. 62, 10109 h (1965).

An aq. slurry of Zn0 is used to absorb $S0_2$ from a gas contg. $S0_2$. The $ZnS0_3$ formed in the slurry is allowed to settle to the bottom, separated, dried at 190°, and calcined at 400°-500° to liberate $S0_2$ and regenerate the Zn0.

123. Peisakhov, I.L. Zinc method of concentration of sulfur dioxide. Sbornik 1953, 20-33; C.A. 52, 1564 i (1958).

The $S0_2$ in smelter gas is absorbed in a slurry of Zn0, forming insoluble $ZnS0_3$. The latter is filtered off and heated to 300-350° to decompose back to $S0_2$ and Zn0. This method has the advantages of operating without necessity of cooling the gas and without interference by the presence of Se. in the gas. There is some $ZnS0_4$ formed which can be recovered from the Zn0 before it is reused.

124. Srbek, J., Klimecek, R., & Jaeger, L. Scrubbing sulfur dioxide from waste gases. Czech. Pat. 108 093, Aug. 15, 1963 (appl. Apr. 13, 1956); C.A. 60, 6524 h (1964).

The $S0_2$-contg. gas is scrubbed with a slurry of Zn0 which is thereby converted to $ZnS0_3$. The $ZnS0_3$ is treated with H_2S0_4 to liberate $S0_2$. The $ZnS0_4$ thus formed is calcined to give Zn0 and $S0_2$. The Zn0 is recycled as a slurry in the absorption step.

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125. Anon.-1968. Developments in desulfurization of waste gas. Sulphur (London) No. 78, Sept.-Oct. 1968, p. 33-34.

Two pilot plants are being built to test the active-carbon adsorption process and the MnO_2 adsorption process. Each pilot plant has a capacity of 150,000 cu. m./h. of flue gas. One at Goi, Japan, using Hitachi Mfg. Co.'s active-carbon adsorption process; the other at Yakkaichi, Japan, using Mitsubishi Heavy Inds. Ltd.'s dry Mn oxide adsorption process.

126. Anon.-1967. Coke cleans flue gas in German process. Chem. Eng. 24, Oct. 23, 1967, p. 94, 96, 98. (cf. ref. Frankenberg).

The Reinluft process for SO_2 removal from waste gases is described with a flow diagram. Capital costs and operating costs are estimated.

126a. Anon. -1969. Specially developed coke is the key feature of a new process to remove sulfur dioxide. Chem. Eng. 76, July 28, 1969, p. 67.

A process has been developed in Germany by Bergbau Forschung GmbH, based on the adsorptive power of certain forms of coke prepared from bituminous coal and subsequently treated with metal oxides. It is said that plans are under way to use this process to recover SO_2 from the flue gas estimated at 3.5 million SCF/h. from a power plant.

127. Anon. -1967. Japanese rushing to cut SO_2 pollution. Oil & Gas J. 65, June 26, 1967, p. 53-54.

Hitachi Mfg. Co. Ltd. is operating a 5 million SCF flue gas per day based on adsorption of SO_2 on active carbon. In the regenerating step, the pregnant carbon is washed with water recovering a H_2SO_4 solution.

128. Brauer, L.W. (to Auergresellschaft Gmbh, Berlin, Germany). Sulfur dioxide absorbent. U.S. Pat. 3 396 122 (Cl. 252-428). Aug. 6, 1968, (appl. Nov. 17, 1964).

A SO_2 absorbent is specified consisting essentially of granular activated carbon impregnated with an alkaline material and 3-10% glycol or 0.5-3.0% polyvinyl alcohol operated at about 28°C.

129. Frankenberg, T.T. (Am. Elec. Power Service Corp., N.Y.) Removal of sulfur from products of combustion. Proc. Am. Petr. Inst. Vol. 45, Sec. III p. 365-370 (1965). (Chemico reprint 2955, p. 367.)

The Reinluft process was invented in the late 1950's by Dr. F. Johswich of West Germany. The Wolkswagen Co. and two other companies are installing it with government subsidy. The process involves adsorption of SO_2 on the char made from peat, size, 10-12 mm. The reactor has 3 zones, vertically disposed and in countercurrent relationship with the reacting gases. In the reactor the char descends slowly at about 1-2 mm. per min. The upper zone operates at 203°-212°F., the middle zone at 320°F., and the lower zone is the desorption zone. The 3 zones are sealed from each other automatically by the char. The waste gases contg. SO_2 enter at the bottom of the middle zone and go upward. The stripping gases, N_2 or CO_2 or a mixt. of the two, at 750°F., enter at the bottom of the lower zone. SO_2 is driven out through the outlet at top of the lower zone in a concn. approx. 50% SO_2. The regenerated char is recycled to the top of the reactor.

130. Juntgen, H. (Berzbau-Forschung GmbH, Germany). The dry process for separating sulfur dioxide from waste gases. Chem.-Ing.-Tech. 38, 734-6 (July 1966).

A simple method to remove SO_2 from waste gases is to use a dry adsorption method with a carbanaceous adsorbent. The latter may be regenerated by washing with water or by applying heat.

131. Kurel, M., Juentgen, H., & Dratwa, H. (to Bergwerksverband Gmbh., Essen, Germany). Method of purifying gases. U.S. Pat 3 345 125 (Cl. 23-2) Oct. 3, 1967, (Ger appl. Nov. 13, 1965).

SO_2 in the flue gas is removed by adsorption on active carbon impregnated with 1-10% Cu, Cr, Fe, Mn, or Ce sulfate or $CoNO_3$ at 100°-160°C. The adsorbent may be regenerated by heating to 300°-500° or higher temp. in a current of inert gas contg. less than 1% O_2.

132. Peters, W., and Juntgen, H. (to Firma Bergwerksverband GmbH., Essen, Germany). Method and apparatus for purifying gases. U.S. Pat. 3 405 508 (Cl. 55-73) Oct. 15, 1968 (German Appl. Oct. 8, 1965).

SO_2 in flue gas is adsorbed on activated carbon or char. The pregnant carbon is next washed with aq. NH_3 and the carbon reused.

133. Tamura, Z., and Hishinuma, Y. (to Hitachi, Ltd., Japan). Method of and Apparatus for Desulfurizing Industrial Waste Gases. U.S. Pat. 3 398 509 (Cl. 55-73) Aug. 27, 1968 (Japanese appl. Aug. 15, 1966).

Waste gases containing small amounts of S oxides are passed through a moving bed of active carbon which adsorbs the S oxides. The pregnant carbon granules are then washed with water to remove the S oxides. From the wash water the S oxides are recovered as dilute H_2SO_4.

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134. Sté.Nationale des Pétroles d'Aquitaine (Mathieu, P., inventor). Catalyst regeneration. Fr. Pat. 1 448 829 (Cl. B O1; C 01b) Aug. 12, 1966 (Appl. Apr. 27, 1965); C.A. 66, 59305 n (1967).

An Al_2O_3 (97%) catalyst used in desulfurizing a gas contg. SO_2 and H_2S was regenerated by heating at 500° for 1 hr. After 18 cycles the catalyst lost only 15% of its initial activity. An identical catalyst regenerated by passing air over the catalyst at 450° rapidly lost activity.

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135. Anon.-1967. Pollution cost gap. Chem. Week 101, July 22, 1967, p. 73-6.

A process flow diagram for the Alkalized Alumina process of the U.S. Bur. of Mines is shown.

136. Bienstock, D., Field, J.H., & Myers, J.G. Process development in removing sulfur dioxide from hot flue gases. (In four parts.) Parts 1 and 3 U.S. Bureau of Mines, RI-5735, 1961. 29 pp; RI-7021, July 1967, 52 pp.

Results are reported of laboratory investigations of absorption of SO_2 at concentrations less than 0.5% in waste gases by metal oxides, expecially Mn oxides and alkalized alumina. (See also abstract under ref. 137.)

137. Bienstock, D., Field, J.H., & Myers, J.G. (U.S. Bur. Mines, Pittsburgh, Pa.) Removal of sulfur oxides from flue gas with alkalized alumina at elevated temperatures. ASME J. Eng. for Power 86, A, 353-8 discussions p. 358-60 (1964); C.A. 61, 7978 h (1964).

The Alkalized Alumina process developed by U.S. Bur. Mines is described. The absorbent is an activated solid compound prepared from Na_2CO_3 and $Al_2(SO_4)_2$. It absorbs both SO_2 and SO_3 and also catalyzes oxidation of SO_2 by O_2 present in the flue gas. Flue gas may be treated with this absorbent in a tower with freefalling absorbent granules or pellets. The spent absorbent is regenerated by passing CO and/or H_2 over it at 600°C. The effluent of the regenerator contains all the S values chemisorbed on the absorbent, in the form of H_2S. A pilot plant including a pulverized-coal firing furnace (2-4 lb. coal burned per h. and producing 500-1000 cu. ft. of flue gas) is described with a process flow diagram and operating data in 5 tables and 7 graphs. When the absorber was operated at 330°C. on a flue gas contg. 0.3% SO_2 and about 6% O_2, with gas linear velocity 8 ft./sec., the absorbent/gas ratio was 3 lb/1000 cu. ft. The SO_2 absorption efficiency was 100% in a absorption tower 25 ft. high, but only 75% in a tower 12.5 ft. high. The presence of fly-ash in the flue gas did not affect the absorption efficiency, nor did it impair the activity and physical characteristics of the absorbent over a long period of continuous operation; and attrition is negligible. The H_2S in the effluent of the regenerator which was operated with a fixed bed may be passed through the Claus reactor using bauxite catalyst to recover elemental S.

138. Field, J.H, Kurtzrock, R.C., & McCrea, D.H. (U.S. Bur. Mines, Pittsburgh, Pa.) How to prevent SO_2 emission. Chem. Eng. 74, June 19, 1967, p. 158-160.

An installation of U.S. Bur. of Mines' alkalized alumina process for SO_2 recovery has been in operation at the power plant at Bruceton, Pa., since May, 1967. It treats 920 SCF flue gas per min. At a boiler load of 90%, it removes 90% of the SO_2 in the flue gas. The power plant is rated at 800 MW. at full load, and the cost of the SO_2 recovery unit was $475,000. The operating cost of the unit is $0.75-$1.00 per ton of coal burned, including a credit for the byproduct sulfur. A process flow diagram is shown.

139. Pijpers, F.W. and Starmans, M.M.J.J. (to Shell Oil Co., N.Y.,N.Y.) Method of removing sulfur dioxide from gases. U.S. Pat. 3 411 865 (Cl. 23-2) Nov. 19, 1968 (Dutch appl. Oct. 3, 1963) (cf. ref. 213).

The alkalized-alumina process for the removal of SO_2 from flue gas may be improved by adding a small amount of Fe oxide and/or Sb oxides to the solid absorbent. The benefit of the presence of Fe and/or Sb oxides is that the rate of regeneration is very much increased so that the whole process becomes more rapid and more efficient.

140. Pijpers, F.W. and Starmans, M.M.J.J. (to Shell Oil Co., New York, N.Y.) Alkali on a support promoted by iron or iron and antimony in sulfur dioxide removal. U.S. Pat. 3 428 575 (Cl. 252-464) Feb. 18, 1969 (Dutch appl. Oct. 3, 1965). (See abstract of ref. 139).

140a. Pigache, P. Recovery of sulfur and sulfur compounds from gases. Brit. Pat. 743 172, Jan. 11, 1956; U.S. Pat. 2 747 968, May 29, 1956; C.A. 50, 13388 a, 16082 b (1956).

S compds. are removed from gases by passing the mixt. through a fixing agent maintained at 100-300°. The fixing agent, which consists of finely divided Cu or oxide on a carrier of Al_2O_3 free of Si, is regenerated by heating to 350-850° and oxidizing with air, followed by reduction with H_2 or CO. The S may be recovered as elemental S, liquid SO_2, or H_2SO_4.

140b. Shell Internationale Research Maatschappij NV. Removal of sulfur dioxide from gaseous mixtures and acceptors for use in the process. Fr. Pat. 1 448 396, June 27, 1966 (appl. Sept. 3, 1965).

A process for SO_2 removal from flue gases is specified, in which the SO_2, together with SO_3, is chemisorbed by a Cu oxide-based "acceptor" supported on silica-alumina. The acceptor is prepared by impregnating silica-alumina with an aq. $Cu(NO_3)_2$ soln. which also contains Cr as a promoter and Ba as a stabilizer. A typical acceptor contains, by weight, Cu 18, Cr 5, Ba 0.5 and silica-alumina 100 parts. The silica-alumina contains silica 87 and alumina 13 wt. % with a specific area not less than 100 sq. m. /g. The gas to be treated must contain sufficient free O_2, so that the chemisorbed SO_2 on the acceptor is completely oxidized to form $CuSO_4$. The absorption is carried out at 325-425°C. in a continuous process by a known technique, such as the fluidized bed system. The pregnant acceptor is then transferred to a regenerator where a reducing gas containing CO and/or H_2 or CH_4, passes over the acceptor at 350-450°C., when the $CuSO_4$ is converted back to CuO and the sulfur values emerge as SO_2, H_2S and S vapor. These are recovered by known methods. After the regeneration, there is a supplementary step whereby a gas containing free O_2 is passed over the acceptor at about the same temperature as in regeneration, so that any over-reduced Cu, and possibly some Cu_2S are reoxidized to CuO. It is claimed that the activity of the specified acceptor improves after the first several cycles of SO_2 absorption and regeneration, and that since the regeneration temperature is only a little higher than the absorption temperature, the stress developed in the acceptor granules is very small, therefore, the life of the acceptor is long (e.g. several hundred cycles without appreciable decrease in activity).

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141. Anon. -1968. Waste gas desulfurization to become practical. Japan Chem. Wk. 9, June 27, 1968, p. 3; Sulphur (London) No. 78, 33-34 (Sept. -Oct. 1968).

The SO_2 removal process developed by Mitsubishi Heavy Inds. is being tested in a pilot plant at Chubu Elec. Co's Yokkaichi power station at a gas rate of 150,000 cu. m./h. The process involves absorption of SO_2 by solid Mn oxide. The SO_2 removal efficiency was about 90%.

142. Anon. -1967. Manganese nodules can provide a cheap way to clean stack gases. Chem. Eng. 24, July 31, 1967, p. 33; cf. Zimmerley, S.R. U.S. Pat 3 330 096 (1967).

After 6 years of development work at Kennecott Copper Corp. Mn nodules gathered from ocean bottom in their natural state was found to react rapidly with SO_2 forming Mn sulfate. The Mn nodules are regenerated by flushing them with water which removes the Mn sulfate. The nodules can be thus used in 10 or more cycles of absorption and regeneration.

143. Anon. -1967. Japanese rushing to cut SO_2 pollution. Oil Gas J. 65, June 26, 1967, p. 53-54.

Mitsubishi Heavy Inds. Ltd. has completed a pilot plant based on absorption of SO_2 by active Mn oxide powder. It has a capacity of 2.5 million SCF flue gas per day.

144. Aktiengesellschaft fur Zinkindustrie vorm. Wilhelm Grillo. Removal of sulfur compounds from flue gases. Neth. Pat. Appl. 6 601 639 (Cl. B 01d) Aug. 11, 1966 (Austrian appl. Feb. 10, Nov. 25, 1965); C.A. 66, 12305 d (1967)

(Continued next page)

ont'd 144. The method described uses a moist, powd., or granulated absorbent const'g of a mixt. of an alkali metal or alk.-earth metal hydroxide and an oxide of Mn, Fe, Al, or Zn deposited on a porous carrier. The amphoteric metal oxides are the active components of the absorbent; the other metal is only present to protect the active ingredients during regeneration by the formation of manganates, aluminates, etc. Example: 124 kg. 70% Mn ore is treated with 500 kg. 50% H_2SO_4. SO_2-contg. flue gases are blown through the mixt. To the almost clear soln. is added 136 kg. of a burned magnesite (90% MgO). Air is blown into the mixt. to oxidize any dissolved Fe. Acid is added to a pH 2-3. A MgO dispersion is then added to pH 4.5-5 and the ppt. (SiO_2 and $Fe(OH)_3$) is filtered. The soln. is vacuum concd. and cooled. The crystals obtained by centrifugation have the compn. $3MgSO_4 \cdot 7H_2O$ + $1MnSO_4 \cdot 7H_2O$. Regeneration is as follows. 500 kg. of the pregnant absorbant and 125 kg. finely ground coal is fed to a rotary furnace held at 900°. Desulfurization begins at once. Steam and just enough air are introduced to maintain a hot reducing atm. in the furnace. All S compds. are reduced to S, H_2S, or COS. These products are then burned to form SO_2 and the gas (12-15% SO_2) is sent to a H_2SO_4 plant. In the oxidizing section of the furnace, more air is introduced; Mn_2O_3 is oxidized to MnO_2, and any remaining S is removed during this stage. To ensure completion of the manganite formation, the hot manganite (≧700°) is quenched with water and hyeroxides of Mg and Mn are formed in this process. The hydroxides are filtered and used as absorbent.

145. Bienstock, D., & Field, J.H. (to U.S. Dept. of Interior). Removal of sulfur dioxide from gases. U.S. Pat. 3 150 923 (Cl. 23-2) Sept. 29, 1964 (Appl. Jan. 18, 1962; C.A. 61, 16694 d (1964).

SO_2 from waste gases was adsorbed on MnO_2 and the SO_2 then released from the spent absorbent $MnSO_4$ to regenerate MnO_2 for recycling in the process. Thus to a 30% soln. of $MnSO_4$ a 25% soln. of NaOH was added in an amt. equal to 20% excess of NaOH. Both solns. were heated to 70° before mixing. The ppt. obtained was washed with cold H_2O dried at 108° for 47 hrs., heated with air for 2 hrs. at 300° and then in vaccuo at 300-40° for 20 hrs. The absorbent thus prepd. contained (wt. %); Mn_2O_3 99, Na_2O 0.4, SO_3 0.5. This was treated as a fixed bed with a simulated flue gas of the following compn, ; (wt. %) SO_2 0.3, CO_2 13.0, O_2 6.0, H_2O 6.7, N_2 74.0. The following absorptions were obtained (temperature, g. SO_2/100 g. absorbent, vol. SO_2/vol. absorbent) 130, 33, 75; 330, 43, 100.

146. Fuller, H.C. (to the U.S. Dept. of the Interior). Process for decomposing manganese sulfate to form manganous oxide and sulfur dioxide. U.S. Pat. 3 301 634 (Cl. 23-145) Jan. 31, 1967 (Appl. July 9, 1963); C.A. 66, 77832 t (1967).

A feed mix consisting of $MnSO_4$ and 4% coal was continuously fed into an externally heated lab-size rotary kiln furnace. The retention time in the hot zone was 20 min. Air was excluded from the interior of the rotary kiln. Roasting the charge at 700° eliminated 79.4% of the S. The product assayed 53.4% Mn and 8.9% S. The evolved gas contained 64.5 SO_2, 7 CO_2, 4 CO, and 0.2% O.

147. Lugwid, S. (World News, Tokyo, Japan). Antipollution process uses absorbent to remove SO_2 from flue gases. Chem. Eng. 75, Jan. 29, 1968, p. 70-72.

The Mitsubishi Heavy Inds. Ltd. process of removing SO_2 with solid Mn oxides in the gas stream at 212°-356° F. is described with a flow diagram.

148. Slack, A.V. (TVA) Air pollution: the control of SO_2 from power stacks. Processes of recovering SO_2. Chem. Eng. 74, Dec. 4, 1967, p. 188-196.

The mitsubishi Heavy Inds. Ltd's process is briefly described with a flow diagram. SO_2 in the flue gas is absorbed by solid Mn oxide in the powder form, which is injected into the flue gas stream upstream from the stack. The Mn oxide with absorbed SO_2 is then separated from the gas stream by mechanical means. About 90% of this Mn oxide power is recycled. About 10% of it is diverted and treated with water which dissolves the Mn sulfate formed in the process and forms a slurry with the Mn oxide. The Mn oxide slurry passes down through a regenerator column with air and NH_3 gas injected into the column to convert the Mn sulfate into $(NH_4)_2SO_4$ and Mn to the desired oxide form. The Mn oxide is then filtered and dried and reused as absorbent. The advantages of this process are (1) gas temp. drops only 20° to 55°F.; (2) low pressure drop through the system, and (3) long life of the absorbent.

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149. Anon.-1969. Another SO_2-removal method. Chem. Eng. News 47, June 2, 1969, p. 39; Chem. Week 104, May 31, 1969, p. 71.

SO_2 in the flue gas is removed to the extent of 70% by injecting powdered nahcolite (a natural mineral containing $NaHCO_3$) into the gas stream. The solid particles are converted to Na_2SO_4 which is collected by means of fabric filters.

150. Ehrenberg, W. Filter-mass for the SO_2 removal from waste gases. Chem. Ing. Tech. 38, (July, 1966). (Chemico transl. TR390).

SO_2 in waste gases contg. CO_2 such as the flue gas from power plants may be removed by contacting the waste gases with porous solid $NaHCO_3$ slightly moistened with water.

151. Martin, D.A., & Brantley, F.E. Selective adsorption and recovery of sulfur dioxide from industrial gases by using synthetic zeolites. U.S. Bur. Mines Report of Invest. 6321, 1963, 15 pp.

Synthetic zeolite of types 4A and AW 500 may be used to adsorb SO_2 from gases provided the gases have been cooled and dried before contacting with the zeolite. The desorption may be carried out at 375^{o} in a current of N_2.

152. Anon.-1968. Two processes offer economic recovery of SO_2 from stack gas. Chem. Eng. News 46, July 8, 1968, p. 13.

(1) Southwest Research Inst., Houston, Texas uses U.S. Bur. Mines alkalized alumina process, but substitutes Na aluminate for alkalized alumina. (2) North Am. Rockwell Co. uses the molten carbonate process (cf. Ibid. 45, Aug. 14, 1967, p. 11). Operating costs of the two processes are estimated based on pilot plant data.

153. Anon. - 1967. Atomic International process of removing $S0_2$ from flue gases. J. Commerce (New York) Aug 9, 1967, p. 9; Chem. Eng. News 45, Aug. 14, 1967, p. 11-12.

The hot flue gas is scrubbed with a molten salt which absorbs $S0_2$. The pregnant molten salt is regenerated when it gives off H_2S. The H_2S is subsequently converted to elemental S by known methods.

154. Heredy, L.A., McKenzie, D.E. & Yosim, S.J. (to N.A. Rockwell Corp.) Removal of sulfur oxides from flue gas. U.S. Pat 3 438 722 (Cl. 23-2) April 15, 1969 (appl. May 15, 1967).

SO_2 in the flue gas is removed by passing the gas in contact with a mixture of alkali metal carbonates at a temp. above $350^{o}C$. Metal sulfites are formed in the molten mixture. The pregnant melt is treated with a mixed gas containing H_2 and CO_2 at 500^{o}. The metal sulfites are thus reacted to form metal carbonates and H_2S. The H_2S is recovered and the metal carbonates reused as SO_2 absorbents. An example of the mixture of metal carbonates is given consisting of LiCL-KCl entectic (LiCl 58 mole % KCl 42 mole % m.p. $348^{o}C$.) 40 g. Li_2CO_3 10 g. and KCl 5.34 g.

155. Beutner, H.P., Niessen, W.R., Haley, M.E. & Emerson, W.S. (Arthur D. Little, Inc.) "Feasibility of a regenerative high temp. amine absorption process for the control of sulfur dioxide emissions from stack gases." U.S. Nat'l Center for Air Pollution Control, Washington, D.C., Aug. 1968, 88 pp; Clearinghouse PB 180 233, $3.00.

An investigation has been made of the removal of SO_2 from hot flue gases without cooling by absorption in aqueous solutions of amines such as triethanolamine. Tetraethylene pentamine, pentahydroxyethyl-diethylenetriamine, and hexahydroxyethyl-triethylenetetramine. It was found that although these amines have high absorptive capacities for SO_2, permanent compounds such as dithionate, trithionate and pentathionate are formed at the high temperatures of the flue gas, so that regeneration of the absorbent is not simple but requiring one of the more elaborate procedures, such as ion-exchange, precipitation, reduction or oxidation, or electrolytic regeneration. Costs of each of these procedures are estimated.

156. Bodoni, D. (to Bodoni & Co. G.m.b.h.) Recovery of carbon dioxide and sulfur dioxide from combustion gases. Austrian Pat. 174 896 May 11, 1953; C.A. 47, 7780 f (1953).

Gases contg. $C0_2$, and $S0_2$ are scrubbed with an aq. soln. contg. N (OET)$_3$, NH_2 (OET) and K_2C0_3 in the ratio 2:2:1 in which the $C0_2$ and $S0_2$ dissolves. The pregnant soln. is regenerated by heating to liberate $C0_2$ and $S0_2$. Recoveries of 95-98% of the $C0_2$ and $S0_2$ in the gases can be made.

157. Kulcsar, G.J., & Lengyel-Szabo, (Univ. Babes-Bolyai Cluj, Romania). The system sulfur dioxide-aniline. III. Absorption isotherms in aqueous solutions. Studia Univ. Babes-Bolyai, Ser. Chemia 9 (1), 77-83 (1964); C.A. 61, 15403 a (1964).

The absorption of $S0_2$ in aq. solns. of aniline increases with concn. of aniline (3, 9%) in water, decreases with temp. but the rate of absorption increases with temp. when the soln. is free from $S0_2$. A typical case is that a 9% aniline soln. absorbs more than 8 g. $S0_2$ per liter of solution. Even then the absorption efficiency is 98% at 40° and 99% at 60°.

158. Marks, G.W., & Ambrose, P.M. Diethylenetriamine and other amines as agents for the recovery of sulfur dioxide. U.S. Bur. Mines, Rept. Invest. 3339, 41-46 (May 1937); C.A. 31, 6422 (1) (1937).

Aq. solns. of diethylenetriamine and triethylenetetramine are excellent absorbers for SO_2 up to 95°, provided that the difference in pressure of this gas over the amine soln. is high enough. Losses of amine during runs over several days were small. On boiling amine solns. that have been satd. with SO_2, a large part of the gas is liberated. Anal. procedures for detn. of SO_4^{--} and amine in amine solns. contg. SO_2 are given.

159. Stout, J.W. III. Sulfur dioxide-ethanolamine-water equilibriums. Dissertation, Lehigh Univ., Bethlehem, Pa., 1965, 175 pp.; Dissertation Abs. 25 (10) 5817 (1965); C.A. 63 3673 g (1965).

Data on vapor-liquid equilibrium of the systems SO_2-ethanolamine-water are presented.

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160. Giona, A.R. & Pfeifer, G. (Univ. Rome, Italy). Sulfur dioxide absorption in dimethylformamide. Chim. Ind. (Milan) 44, 1354-1361 (1962); C.A. 58 7422 a (1963).

The soly of $S0_2$ in anhy. and aq. DMF was investigated. The isotherms show that soly. decreases with increase in H_20 content in the solvent. The soly. of $S0_2$ at 20° and 760 mm. partial pressure was found to be 470 ml./g. DMF. The data on heat of solution are given.

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161. Smedslund, T.H. Dimethyl sulfoxide as solvent for sulfur dioxide. Finska Kemistsamtundets Medd. 59, 40-43 (1950); C.A. 46, 4329 a (1952); cf U.S. Pat. 2 539 871 (1951).

At 18° a soln. of 60.13% $S0_2$ in $(CH_3)_2S0$ was obtained at atm. pressure. Moderate heat is evolved during absorption of $S0_2$ in $(CH_3)_2S0$ and the volume of the solvent increased from 1 to 2.03. At 100° a saturated soln. contains 17.9% $S0_2$, at 161° 3.2%.

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162. Badische Anilin-& Soda Fabrik AG. (Giesler, E., inventor). Separation and recovery of sulfur dioxide from waste gases. Ger. Pat. 1 191 793 (Cl. C 01b) Apr. 29, 1965 (appl. Dec. 17, 1963); C.A. 63, 6712 g (1965).

The absorbent for the recovery of $S0_2$ from waste gases is specified as an organic polyhydroxy compound, such as glycol, glycerol, or pentaerythritol, either pure or dissolved in water to which $Ca0$ is added. The pregnant liquor contains $CaS0_3$. The solid $CaS0_3$ is separated and calcined to recover $S0_2$ and $Ca0$. $Ca0$ is recycled.

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163. Nobel-Bozel (Marchequet, H. G. L. & Gandon, L., inventors). Extraction of $S0_2$ from gases. Fr. Pat 1 224 892 June 28, 1960; C.A. 55, 20357 a (1961); cf. U.S. Pat 2 994 585 Aug. 1, 1961.

A glyoxal soln. at 15°-30° was used for the solvent. Desorption was carried out by raising the temp. of the solution to 65°-75°.

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164. Nobel-Bozel. (Marcheguct, H. G. L., & Gandon, L., inventors). Sulfur dioxide separation. Fr. Pat. 1 353 646 (Cl. C 01b) Feb. 28, 1964 (appl. Jan. 18, 1963); C.A. 61, 336 e (1964).

$S0_2$ in the stack gas is absorbed in aq. glyoxylic acid, OHC COOH, to form $HOOCCH(OH)S0_3H$. The latter gives up $S0_2$ when heated. No H_2S0_4 is formed.

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165. Kohl, A. L. & Riesenfeld, F. C. Gas purification: $S0_2$ removal by liquid absorption. Chem. Eng. 66, June 15, 1959, p. 147-151.

The following processes are briefly described with flow diagrams. (1) Sulfuridiene process (using aq. 50% xylidine). (2) Asarco process (using dimethylaniline). (3) Cominco process (using $(NH_4)_2S0_3$. (4) Battersea process (using $CaC0_3$ and $MnS0_4$). (5) Zinc oxide process (using Na_2C0_3, Zn0 and $Ca(OH)_2$). In the last process the pregnant soln. is a $NaHS0_3$ soln. because $S0_3$ is capable of displace C[illegible] aq. soln. Zn0 is added to convert $NaHS0_3$ into $ZnS0_3$ an[illegible] calcining $ZnS0_3$ in closed system, a gas contg. 30% $S0_2$ and 70% H_20 is obtained.

166. Lurgi Gesellschaft fur Chemie und Huttenwesen m. b. H. The Sulphidine process. Brochure issued by Lurgi, no date, Chemico reprint No. 732.

An 1:1 aq. soln. of xylidine, $(CH_3)_2C_6H_3NH_2$, is used as the absorbent for low-concn. $S0_2$ in gases. Working with a 0.5% $S0_2$ gas at 20°-25° C. and atmospheric pressure, the $S0_2$ capacity of the absorbent is shown in a graph to be about 90 g. /l. as vs. about 55 g. /l. for basic $Al_2(S0_4)_3$ soln. contg. combined Al_20_3 53.2 g. /l. and free Al_20_3 45.5 g. /l. $S0_2$ desorption is conducted at 100°-102° C. Photos of installations are shown. (Xylidines as 4 isomers boil in the range 216°-226° C. Mixed xylidine is currently quoted at 44¢/lb., in tanks delivered.)

167. Roberson, A.H., & Marks, G.W. Partial pressures of sulfur dioxide over solutions of sulfur dioxide in mixtures of water and various aliphatic amines. U.S. Bur. Mines Rept. Invest. 3415, 45 pp. (Oct. 1938); C.A. 33, 949 (9) (1939).

A comprehensive study of the solvents for SO_2 recovery by absorption and desorption is reported. These solvents include: (1) xylidine, (2) basic aluminum sulfate, (3) $(NH_4)_2SO_3$, (4) diethylenetriamine, (5) triethylenetetramine, and (6) monoethanolamine. The data on monoethanalamine include the compositions (wt. % of MEA, SO_2 and H_2O) of the solns. before and after absorbing SO_2 at various temps. and degree of saturation.

168. Weidmann, H., (Metallgesellschaft A.-G. Germany). The "Sulphidine" process for recovering sulfur dioxide. Ind. Eng. Chem. News Ed. 14, 105 (1936); cf. Dean, R.S., et al., U.S. Bur. Mines, Rept. Invest. 3339, 1937, 51 pp.

SO_2 and SO_3 in a gaseous mixt. is absorbed in a 1:1 mixt. of xylidine and water, adding Na_2CO_3 or Na_2SO_3 to convert any xylidine sulfate into Na_2SO_4 - The pregnant liquor is then heated to 80°-100° to drive off SO_2 in the pure form. To remove Na_2SO_3 whenever an accumulation occurs in the aq. phase, it is a simple matter of replacing a part or all of the aq. phase with fresh water. The xylidine is only slightly soluble in the aq. phase. The initial mixt. of xylidine (a reduction product of nitroxylene) and water is a two-phase liquid mixt. When xylidine absorbs enough SO_2, it becomes xylidine sulfite which is soluble in water. After desorption of SO_2 the mixt. again separates into two liquid phases which settle into liquid layers. Toluidine may be similarly used. When this process was operated at 15-30° on a gas contg. about 7% SO_2, the residual SO_2 in the effluent gas was as low as 0.1%. The efficiency of desorption is better than 99%. Xylidine vapors in the effluent gas amounts to 2.5g per cu. m. at 20-25°, and is recovered by an alkaline bisulfite wash. The desorbed SO_2 gas also contains a small amount of xylidine which is removed by an aq. H_2SO_4 wash.

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169. Robinson Bros. Ltd., Parkes, D.W., & Evans, R.B. Recovering acidic gases from gas mixtures. Brit. Pat. 468 972, July 15, 1937; C.A. 32, 755 (2) (1938).

CO_2, SO_2, and H_2S, etc. are removed and recovered from gas mixtures by scrubbing with an aq. soln. of 1 or more dipiperidyls and subsequently regenerating the scrubbing soln. The dipiperidyls may be made by electrolytic reduction of the corresponding pyridine bases or by reduction of corresponding dipyridyls.

170. Somer, V.H. (to Aktiebolaget Kaukas Fabrik) Concentrating gases containing sulfure dioxide. Norw. Pat. 76 164, May 30, 1949; Swed. Pat. 126 527, Oct. 25, 1949; C.A. 44, 3684c, 3712d (1950).

Gases contg. SO_2 are treated with aq. 2-aminocymol which absorbs SO_2. The SO_2 is recovered by boiling the soln.

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171. Copson, R.L. & Payne, J.W. (Socony-Vacuum Corp., Paulsboro, N.J.) Recovery of sulfur dioxide as dilute sulfuric acid. Ind. Eng. Chem. 25, 909-916 (1933).

It has been found possible to recover sulfur dioxide from waste gases as dilute sulfuric acid. Mixtures of sulfur dioxide and air are bubbled through water containing manganese sulfate as catalyst. A 30% acid is readily produced, but the reaction ceases at about 40% acid. In a glass column with a fine porous plate at the bottom, through which the gas is introduced, rates of absorption several times higher than those reported by Johnstone are obtained. The concentration of catalyst, temperature, gas composition, rate of gas flow, and depth of absorbing solution are studied as affecting the rate of absorption. The capacity of the apparatus is compared for batch as against continuous operation. Other experiments show that the rate of absorption per unit volume is greater with a fine porous plate than with a coarse plate. The rates of absorption per unit volume in both a small and a large packed tower are much lower than those in the glass column with porous plate bottom. The catalyst is susceptible to poisoning by minute amounts of certain substances. In this connection, water from several sources, refinery gases containing sulfur dioxide, and various materials of construction were tested.

172. Johnstone, H.F. The elimination of sulfur compounds from boiler-furnace gases. Proc. 3rd Intern. Conf. Bituminous Coal 2, 576-592 (1932); Ind. Chem. Eng. 23, 559-(1931); Fuel 11, 84-90 (1932); C.A. 26, 2301 (3) (1932).

The possibility of increasing the capacity of H_2O for absorbing SO_2 by the rapid catalytic oxidation of the dissolved gas with dissolved O_2 from the flue gases was studied. Fe and Mn ions show an extremely powerful catalytic effect which is not affected by moderate concns. of acids. There is an optimum concn. of the catalysts above which the catalytic effect decreases, in these expts. 1.2% Fe and 0.025% Mn, which yield resp., 50 and 100 l. SO_2 per l. of soln. With Mn, as much as 5400 cu. ft. per gal. H_2O can be washed with an av. efficiency of 92.2% before the differential efficiency falls to 30% (H_2SO_4 in liquor 45.5%). At the optimum catalyst concen., increasing temp. decreases the acid content at which effieincy falls. As the percentage of O_2 in the gases is progressively decreased, the efficiency is more susceptible to acid concn.; efficiency is less affected by acid concn. with decrease of SO_2 concn. Definite promoter action is shown when a very small concn. of Mn is added to dil. Fe^{+++} solns. When Fe salts are used as catalysts, the

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Cont'd 172. capacity of the soln. is greatly increased by circulation of the soln. over scrap Fe. A no. of compds. act as inhibitors to the catalyzed reaction. The most effective are the phenols, of which those contg. 2 hydroxyl groups are stronger than those contg. 1 (5 ppm will almost stop the reaction). Cu and Sn salts show a negative influence, but with Sn the effect is gradually overcome. H_2S shows no effect up to 0.2% but is an inhibitor above this point. CO, H_2, etc., have no effect. Inhibiting action is much more noticeable with Mn than Fe catalysts.

173. Dr. C. Otto & Co. GmbH. (Struck, C.H., inventor). Removal of sulfur dioxide from industrial gases. Ger. Pat. 1 234 912 (Cl. F 23); Feb. 23, 1967 (Appl. Dec. 2, 1961); C.A. 66, 97014 F (1967).

SO_2 and SO_3 are removed from gases by washing with a 35-80% H_2SO_4 soln. contg. peroxysulfuric acid (I) equiv. to 5-60% g. H_2O_2/l. at a temp. >60° which is also in excess of the dew point of the gas being cleaned. The H_2SO_4 formed is continuously removed and the used I is regenerated by anodic oxidn. The gas may be subjected to previous mech. cleaning and/or be cooled to room temp. and reheated for cleaning. Thus, to clean at 80° a gas having a dew point of 70°, a 5-15 sec. contact with 37% aq. H_2SO_4 contg. the equiv. free O_2 of 20 g. H_2O_2/l. is satisfactory.

174. Simon-Carves Ltd., Parker W.C., & Gillham, E.W.F. Improvements relating to the removal of sulfur dioxide from gases. Brit. Pat. 633 627, Mar. 18, 1950; C.A. 44, 4656 g (1950).

A process is described for the removal of SO_2 from gases in which it occurs in low concns. NH_3 neutralizes the absorbed SO_2, the absorbent used being an acid H_2O_2 soln. and NH_3 causes a reduction and SO_2 an increase in the cond. of the absorbent, so that the result of the cond. measurement indicates whether NH_3 or SO_2 is present in excess in the effluent gases from the washer, or whether the wash liquor is liberating NH_3 or SO_2.

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175. Acs, M., Takacs, P., & Szucs, Z. Utilization of high-voltage electric fields for the desulfurization of fumes. I-II Magy. Kem. Lapja (Budapest) 21, 28-31, 96-100 (1966) (in Hungarian); C.A. 64, 10787 a, 17305 h (1966).

Air contg. 0.3% SO_2 is mixed with NH_3 gas in the molar ratio of NH_3/SO_2 of 2:1, and the mixt. is passed through a dielec.-heated tube at 130° and 5-10,000 volts. The SO_2 combines with NH_3 forming $(NH_4)_2SO_3$ which is oxidized by O_3 which is generated in situ by the high voltage. The resulting $(NH_4)_2SO_4$ drops out of the gas stream.

176. Kashtanov, L.I. Testing the ozone-catalytic method under semifactory conditions. J. Chem. Inc. (USSR) 14, 365-9 (1937); C.A. 31, 6114 (b) (1937).

The oxidiation of SO_2 by O_3 in the presence of $MnSO_4$, studied by K. and Ruizhov (C.A. 30, 7019 (s) (1936)) can be applied to the removal of SO_2 from industrial gases. The apparatus is described.

177. Kuesters, W. Treatment of flue gas. Neth. Pat. Appl. 6 607 238 (Cl. B old) Jan. 10, 1967 (German Appl. July 9, 1965); C.A. 66, 118592 k (1967).

The flue gas rotates in a purification chamber contg. 2 concentric electrods. The external electrode can be a grid., on which the charged particles lose their elec. charge. The elec. field between external and central electrode is chosen so high that corona discharge is obtained. The corona discharge leads to the following chem. reactions. O is converted into O_3; this O_3 converts SO_2 to SO_3. The complete installation is built in corrosion-free material.

178. Nechaeva, N. Removing SO_2 from fuel gas. Novosti Tekhniki, Ser. Gorno-Rudnaya Prom. 1935, No. 41-42, 13; C.A. 31, 2783 (8) (1937).

Fuel gas was completely freed from SO_2 by oxidation in high frequency elec. discharges.

179. Tarbutton, G., Driskell, J.C., Jones, T.M., & Smith, C.M. (to TVA). Recovery of sulfur dioxide from waste gases. U.S. Pat. 2 926 999, Mar. 1, 1960; Ind. Eng. Chem. 49, 392-5 (1957).

The gaseous mixture containing SO_2 is treated with O_3 to the extent of 20-80 ppm. based on gas mixture. Enough O_2 is present in the mixture to satisfy the formation of SO_3 from SO_2. The resulting gas is scrubbed with an aq. solution of H_2SO_4 or $(NH_4)_2SO_4$ containing Mn ion at a temp. below the b.p. of the solution but above the dew point of the gas mixture. The SO_2 in the gas mixture appears in the scrubbing effluent as sulfate ion.

180. Vasilev, S.S., et al. Application of catalysts and ozone in water purification of flue gases from sulfur dioxide. Novosti Tekhnici 1936, No. 58-59, 12-13; C.A. 31, 3666 (s) (1937).

A soln. of Mn salts (0. 1%) used for the absorption of SO_2 results in a 25% H_2SO_4 soln. The action of O_3 in the process of SO_2 oxidation depends on the ratio of O_3 concn. to SO_2 concn. At equal concn. one mole of H_2SO_4 is formed per mole of O_3; if there is a high excess of SO_2, then 15-20 moles of H_2SO_4 is formed per mole of O_3. This is explained by the chain reaction between O_3 and SO_3. Mn is probably a catalyst in this case.

181. Empresa Auxiliar de la Industria S.A. Removal of sulfur oxides. Brit. Pat. 1 037 554, July 27, 1966.

SO_2 in the flue gas is absorbed in a bed of a pyridine polymer resin, which is formed by copolymerizing 2-methyl-5-vinyl pyridine and p-divinyl benzene. During adsorption of SO_2, the resin is in contact with water at 25°-60°. After adsorption, air is blown through the resin bed to oxidize SO_2 to SO_3. Then aq. NH_3 is passed through the resin to produce $(NH_4)_2SO_4$. Finally, the resin bed is eluted with water to recover $(NH_4)_2SO_4$.

181a. Layton, L. & Youngquist, G.R. (Clarkson College of Technol., Potsdam, N.Y.) Sorption of sulfur dioxide by ion-exchange resins. I&EC Process Design & Dev. 8, 317-324 (July 1969).

The ion-exchanger resin used was a polymer derived from the reaction of a secondary amine with a chloromethylated styrene-divinylbenzene copolymer. It is used in the dry state. Some permanent absorption of SO_2 occurred, but that did not interfere with the adsorption capacity of the resin for SO_2 at 25°C. Desorption was carried out at 90°C. At a SO_2 partial pressure of 50 mm Hg, the adsorptive capacity of the resin is comparable to those of active charcoal and zeolite.

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182. Anon.-1968. Monsanto's process to recover sulfur dioxide from power plant stack gases went commercial. Chem. Eng. News 46, Oct. 7, 1968, p. 27; Oct. 14, 1968, p. 53. Chem. Eng. 75, Oct. 21, 1968, p. 47-48. Chem. Week 103, Oct. 5, 1968, p. 120; Oct. 21, 1968, p. 47-48; Europ. Chem. News 14, Oct. 18, 1968, p. 46; Sulfur (London) No. 79, Nov.-Dec., 1968, p. 46; cf. Chem. Eng. News 45, July 10, 1967, p. 28-29.

After operating the SO_2 recovery unit for more than a year at the Metropolitan Edison Co's 800 Mw coal burning power plant, Portland, Pa., Monsanto Co. decided to offer the catalytic oxidiation process (see ref. 198) for licensing. The capital cost for the SO_2 recovery unit is estimated at \$20-\$30 per Kw power-plant capacity.

183. Anon.-1967. Sulfur limits throw utilities in turmoil. Chem. Eng. News 45, July 10, 1967, p. 28-29.

The new power station of Metropolitan Edison Co. has been completed at Portland, Pa., incorporating the Monsanto unit of SO_2 recovery system. The Monsanto process oxidizes SO_2 in the flue gas to SO_3 in the presence of a V catalyst. The SO_3 is then scrubbed with water to give a 70% H_2SO_4.

184. Anon. -1966. Sulfur that gets away. Chem. Week 98, May 21, 1966, p. 26-28; Chem. Marketing (N.Y.) 189, Apr. 25, 1966, p. 5, 34.

SO_2 escaped from stacks in the U.S. is estimated at 21,000,000 tons/yr. If this amount is recovered and made into H_2SO_4, it would be 32,000,000 tons of H_2SO_4, 100% basis. The total consumption of H_2SO_4 in the U.S. is about 24,000,000 tons/yr. Monsanto Co. has developed a process of recovering SO_2 from stack gas. A prototype unit will be installed soon at Metropolitan Edison Co's power station at Portland, Pa. The process uses V_2O_5 catalyst to oxidized SO_2 in the stack gas to SO_3 and the latter is converted to 70% H_2SO_4.

185. Anon. -1966. Saleable ammonium sulfate from SO_2-containing stack gases. Sulphur (London) No. 65, p. 32 (Aug.-Sept. 1966). (cf. ref. 196).

The process developed by Dr. R. Kiyoura of Tokyo Inst. of Technol. comprises catalytic oxidation of SO_2, after which NH_3 is injected into the gas stream to form solid $(NH_4)_2SO_4$ which is recovered by dust collector. Costs of equipment and operating costs are estimated for a 600 Mw. power plant burning fuel oil. At 90% load capital cost is $6,670,000 and operating cost 0.009¢ per Kwh with credit to the by-product $(NH_4)_2SO_4$. SO_2 in flue gas is reduced from 0.2% to 0.02%.

186. Anon. -1966. New pilot plants tackle SO_2 pollution. Chem. Eng. News 44, July 4, 1966, p. 36-38; Sulphur (London) No. 64, 32 (June-July 1966); cf. Brit. Chem. Eng. 11, 641-2 (July 1966).

Six pilot plants are planned or under construction in the U.S. to test different processes of SO_2 removal and recovery from flue gases. A flow diagram is shown, which is similar to the Monsanto process and the Kiyoura-T.I.T. process. The end product of this process is $(NH_4)_2SO_4$ and the residual SO_2 in tail gas is 0.02%.

187. Anon. -1967. Japanese rushing to cut SO_2 pollution. Oil & Gas J. 65, June 26, 1967, p. 53-54.

A pilot plant based on the Kiyoura-TIT process of SO_2 removal is described. It treats power-plant flue gas at a rate of 424 million SCF flue gas per day. It is expected that the data obtained from this pilot plant will enable Dr. R. Kiyoura to design a full-scale unit for standard-size thermal electric power plants. (cf. ref. 196).

188. Anon. -1966. SNPA H_2SO_4 process utilizes sour gas. Europ. Chem. News 10, Aug. 19, 1966, p. 38; Sulphur (London) No. 66, Oct-Nov. 1966, p. 39.

A joint development of Ste. Nat. de Petroles d'Aquitaine (SNPA) and Haldor Topsoe. Feed gas has less than 1% SO_2, product 93% H_2SO_4, recovery 95%, and tail gas contg. 0.0025% (25 ppm) SO_3. A plant with a capacity of 140,000 tons H_2SO_4/yr. is now in operation at ANPA's plant in Lacq.

189. Anon.-1966. New pilot plants tackle SO_2 pollution. Chem. Eng. News 44, July 4, 1966, pp. 36-38.

The Monsanto and Kiyoura-T.I.T. (Tokyo Inst. of Technol.) processes are described with flow diagrams.

190. Anon.-1966. SO_2 removal from flue gases. Brit. Chem. Eng. 11, 641-2 (July 1966).

A flow diagram is shown representing the process developed at Pa. Electric Co. at Seward, Pa., since 1961. This process is similar to the Monsanto process, and the end product is H_2SO_4. The residual SO_2 in the end gas is 0.02% along with 0.002% SO_3, which are acceptable under air-pollution control. The flue gas from the boiler contains 0.20% SO_2 and 0.002% SO_3. The full-scale plant based on this process will be built at Portland, Ore., by Metropolitan Edison Co. (cf. ref. 193.)

191. Anon.-1966. Promise seen in stack-gas SO_2 removal. Oil Gas J. 64, May 2, 1966, p. 53.

Babcock & Wilcox, Inc., and Monsanto Co's processes of SO_2 removal systems are briefly described. Other schemes are mentioned.

192. Anon.-1964. Flue-gas purification unit makes byproduct acid. Chem. Eng. 71, June 8, 1964, p. 92, 94.

The process developed by Tigges of Jackson & Moreland Inc. is described. The process is based on the following steps: (1) removal of dust from hot flue gas by electrostatic pptn.; (2) oxidizing the SO_2 to SO_3 using V catalyst; (3) condensing the H_2SO_4 to form a 70% H_2SO_4, and collecting the H_2SO_4 mist by a second electrostatic pptor. The cost of plant attached to a 1,000,000 Kw power plant burning coal contg. 3% S is estimated at $14,500,000.

193. Bovier, R.F. (Pa. Elec. Co., Johnstown, Pa.) Sulfur-smoke removal system. Paper read at 26th Annual Am. Power Conf., Apr. 16, 1964, Chicago, Ill.

The gas from burning coal contg. 3% S is first treated to remove fly ash. It passes through a V_2O_5 catalyst bed where SO_2 is oxidized to SO_3 by preheated air. The H_2SO_4 mixt. is collected by an electrostatic precipitator. The gas leaving the precipitator contains SO_2 200 ppm and SO_3 20 ppm. 90% of the S in the coal is recovered as 70% H_2SO_4 at a cost of $7.00/ton.

194. Furkert, H. (to Chemiebau Dr. A. Zieren GmbH.) Recovery of products from waste gas. U.S. Pat. 3 129 663, (Cl. 23-175) Jan. 28, 1964 (appl. Jan. 21, 1958); C.A. 61, 333 f (1964).

SO_2 in wastes gas is catalytically oxidized to SO_3. The gas is then cooled to a temp. above its dew point, and the SO_3 is absorbed in 98% H_2SO_4.

195. Guyot, G. (SNPA, France) SNPA process for the treatment of residual gases with low concentration in SO_2. Chim et Ind. Genie Chim. 101, 31-34, 813-6 (Jan., Mar. 1969).

The process is designed to treat the tail gas of the Claus process containing SO_2, H_2S and S vapor, a total of 1.5 vol. %. This gas has also a moisture content up to 30%. The gas is passed over a V_2O_5 catalyst at 540°C to convert the S values into H_2SO_4 without formation of acid mist. The reaction products are scrubbed with 80-85% H_2SO_4. The concn. of the scrubbing acid rises in the process to about 94%. The scrubbing is carried out at 250°-275°C. A process flow diagram is shown. Data from pilot plant tests show: the feed gas contained SO_2 1%, H_2S 1%, moisture 11%; conversion of S compounds to SO_3 was 90-95%; product acid was 94% H_2SO_4; emission of SO_3 in the tail gas was 75 mg/cu. m.

196. Kiyoura, R. (Inst. Technol., Tokyo, Japan). Removal of SO_2 from hot flue gases to prevent air pollution. J. Air Pollution Control Assoc. 16 (9), 4688-9 (1966); C.A. 65, 20739 c (1966).

SO_2 in flue gas is catalytically (V_2O_5) oxidized to SO_3. The small amount of moisture in the gas converts the SO_3 to H_2SO_4. Then NH_3 gas is injected into the hot gas stream to form solid $(NH_4)_2SO_4$ which is collected with the fly ash in a cyclone.

197. Pauling, E. (to Metallgesellschaft AG., Frankfurt am Main, Germany). Sulfur dioxide separation. U.S. Pat. 3 318 662 (Cl. 23-168) May 9, 1967 (Germ. appl. Oct. 17, 1960).

Small amounts of SO_2 in gases are removed from gases containing it by a catalytic process at a temp. between 20° and 100°C. The catalyst is either V_2O_5 or similar material supported on active carbon, or an active carbon containing 0.1 to 5% I_2. The gases to be treated would contain water vapor and excess O_2, so that H_2SO_4 is formed and subsequently removed from the catalyst.

198. Remirez, R. (ed) Catalytic route is ready for flue-gas cleanup jobs. Chem. Eng. 76, Apr. 21, 1969, p. 86-88.

(Continued next page)

Cont'd 198. The Monsanto process of SO_2 removal by catalytic oxidation as installed at Metropolitan Edison Co's Portland, Pa., 250 Mw power plant is described with a flow diagram. The catalyst works with hot flue gas and removes about 90% of the SO_2 in the gas. Even if temp. of the gas should drop to 175°F., as when the power plant is operating at 50% boiler load, the SO_2 removal is still as much as 80%. A byproduct of H_2SO_4 with a strength of about 80% is obtained.

199. Terminet, R. (to Société Nationale des Pétroles d'Aquitaine, France). Catalyst composition and process for the recovery of sulfur compounds from gas mixtures. U.S. Pat. 3 300 280 (Cl. 23-175) Jan. 24, 1967 (France appl. Feb. 11, 1963).

The catalyst is alumina-based containing about 6% V_2O_5 and 7-8% K_2O. Operating temp. is 430° and contact time 0.25-0.35 sec. In the presence of O_2 SO_2 at low concn. is oxidized to SO_3 which is subsequently removed by absorption in water or conc. H_2SO_4.

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200. Anon.-1968. SO_2 removal: Cheaper process piloted. Chem. Eng. News 46, Sept. 9, 1968, p. 22.

The Princeton Chemical Research, Inc. has developed a process, called PCR process, to remove SO_2 from waste gases by a series of catalytic reactions: (1) Elemental S is reacted with natural gas and steam to produce H_2S and CO_2. (2) the H_2S is reacted with SO_2 to produce elemental S, and a part of this S is reacted with natural gas and steam to produce H_2S (as in step (1). The main part of elemental S is a saleable byproduct.

201. Spence, P. & Sons Ltd. Sulfur dioxide removal. Belg. Pat. 661 381 July 16, 1965 (Brit. appl. Feb. 5, 1964); C.A. 65, 6792 a (1966).

With about 90% of the stoichemetric amount of H_2S supplied, the Claus process: $SO_2 + 2H_2S \rightarrow 3S + 2H_2O$ may be used to eliminate SO_2 from flue gases. Example: In the presence of activated Al_2O_3 as catalyst, operating at 50°-300°, elemental S deposits on the catalyst, and the gas coming out of the reactor contained no SO_2. Starting from a gas contg. 0.24% SO_2, all of the SO_2 was eliminated in about 1.65 sec. Presence of CO_2 (1%), O_2 (20%), and H_2O vapor (6%) did not interfere with the process.

202. Sulfur-Chemie A.-G. Purifying gases. French Pat. 804 487, Oct. 24, 1936; C.A. 31, 3671 (7) (1937).

Gases contg. SO_2 is passed together with an equivalent amount of H_2S into an aq. soln. contg. oxygenated compounds of thiosulfate. This promotes the reaction between SO_2 and H_2S with pptn. of elemental S.

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203. Beckman, J.W. Purifying sulfur dioxide containing gases. U.S. Pat. 2 090 828, Aug. 24, 1937; C.A. 31, 7628 (3) (1937).

SO_2 in gases is eliminated by adding CO, H, or CH_4 to the gas and contact the mixt. with porous lime heated to 400° so that SO_2 is reduced to elemental S which is then removed by filtration.

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204. Anon.-1967. Dry chromatographic process for recovering sulfur oxides. Sulphur (London) No. 72, Sept.-Oct. 1967, p. 28.

The process is now being developed by Dr. A. Teller of Cooper Union, N.Y.

205. Arne, F. (ed.) Heady days are here for sulfuric acid producers. Chem. Eng. 73, Apr. 25, 1966, p. 104-6, 108.

The contact H_2SO_4 plant exhaust gas contg. residual SO_2 may be treated by a process developed by Aaron Teller, dean of engineering at Cooper Union, N.Y., which is based on the principles of mass transfer similar to those involved in gas chromotography.

206. Pollard, F.H., Hanson, P., & Nickless, G. (Univ., Bristol, England). Chromatographic studies on the oxidation of sulfurous acid by ferric iron in aq. acid solution. J. Chromatography 5, 68-73 (1961); C.A. 56, 6879 a (1962).

Using the chromatographic technique, SO_2 is oxidized by Fe^{+++} ion to the dithionate ion: (1) $SO_2 + H_2O + Fe^{+++} \rightarrow Fe^{++} + HSO_3 + H^+$ (2) $SO_2 + HSO_3 + Fe^{+++} + H^+ \rightarrow Fe^{++} + H_2S_2O_6$. Almost quantitative oxidation of H_2SO_3 occurs with increasing H_2SO_3/Fe^{+++} ratios.

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207. Anon.-1969. A new way to cut sulfur dioxide emission form sulfuric plants. Chem. Week 105, July 19, 1969, p. 52; (cf. ref. 89.)

Olin Mathieson Chem. Corp. has recently contracted Wellman-Lord Eng. Inc. to install a SO_2 removal unit in conjunction with the existing 700 tons/day H_2SO_4 plant at Paulsboro, N.J. with the object of reducing the SO_2 content of the tail gas from 1800-2000 ppm. down to 500 ppm. Wellman-Lord has not revealed the nature of the SO_2 removal process except that it uses an aq. salt solution to absorb SO_2.

208. Anon. -1967-1968. The Wellman-Lord SO_2 recovery process. Sulphur (London) No. 73. Nov. -Dec. 1967, p. 24-27; No. 79, Nov. -Dec. 1968, p. 46-47; cf. ref.

Wellman-Lord Co. has developed a process (no information about the chemistry of it is disclosed) to remove and recover SO_2 from stack gas. Capital costs and operating costs are estimated. An installation is now under construction at Baltimore Gas & Elec's power station in Maryland.

209. Anon. -1968. Desulfurization for thermal power stations. Look Japan 12. Mar. 10, 1968, p. 20-21.

A review of processes for the removal of SO_2 from flue gas in Japan.

210. Anon. -1967. Desulfurization: Coal and flue gas. Sulphur (London) No. 73, Nov. /Dec. 1967, p. 20-23.

The various processes for the removal of SO_2 from flue gases are briefly described. The estimated capital and operating costs for the Mitsubishi Heavy Inds. Ltd's DAP-Mn process are given.

211. Anon. -1967. Removal of sulfur dioxide from flue gases. Sulphur (London) No. 68, Jan. -Feb. 1967, p. 24-29.

The following process for the removal of SO_2 from flue gas briefly described with flow diagrams: (1) Simon-Carves NH_4SO_3 process; (2) Mitsubishi's aq. Mn oxide slurry scrubbing process; (3) Kiyouro-TIT process; (4) U.S. Bur. Mines' alkalized alumina process; (5) the Reinluft process, and (6) the Jecco lime-gypsum process. The estimated capital and operating costs for the Kiyoura-TIT process are given.

212. Anon. -1967. Stack-gas sulfur may be boon to fertilizers. Chem. Eng. News 45, Sept. 18, 1967, p. 72, 74.

Processes and pilot plant operations are tabulated.

213. Anon. -1967. Removal of sulfur dioxide from flue gases. Sulphur (London) No. 68, Jan. -Feb. 1967, p. 24-29.

The following processes of SO_2 removal are described with flow diagrams: (1) $(NH_4)_2SO_3$ solution; (2) Mitsubishi's $MnSO_4$ solution; (3) Monsanto's catalytic oxidation; (4) Kiyoura's catalytic oxidation; (5) U.S. Bur. Mines' alkalized alumina; (6) Central Electricity Generating Board's fluidized sodium aluminate process (UK); (7) Shell alkalized alumina process; (8) Reinluft process (Germany), and (9) Jecco lime slurry process (Japan). Estimated capital and operating costs are given.

214. Frankenberg, T. T. (Am. Elec. Power Service Corp., N. Y., N. Y.). Removal of sulfur from products of combustion. Proc. Am. Petro. Inst. Sect. III. 45 (3), 365-370 (1965); C. A. 65, 15972 d (1966).

Available processes for removal of SO_2 from stack gases are reviewed. In none of the processes is the recovery of byproduct S compounds economical.

215. Johswich, F. The present position of flue-gas desulfurization. Breunstott-Waerme-Kraft 17 (5), 238-245 (1965) (in German); C. A. 63, 8071 c (1965).

The following processes are reviewed and the costs of S recovery compared: Reinluft process (adsorption on C), Penelec process (catalytic oxidation), Wickert process (injection of powdered dolomite), Bayer-Leverkusen process (a 2-step process involving catalytic oxidation), the alkalized Al_2O_3 process. Processes involving scrubbing with aq. soln. and slurries such as ZnO slurry are considered "impractical on a large scale."

216. Katell, S. (U.S. Bur. Mines) Removing sulfur dioxide from flue gas. Chem. Eng. Prog. 62, Oct. 1966, pp. 67-73

Three dry processes for SO_2 removal from flue gases are compared based on a power plant of 800 Mw capacity burning coal containing 3% S. These processes are (1) Alkalized alumina (U.S. Bur. Mines); (2) Reinluft (German), and (3) Catalytic oxidation (Monsanto Co.) The capital cost is lowest for (1) and highest for (3). The operating cost at 90% load is lowest for (3) provided the byproduct of 70% H_2SO_4 can be utilized locally. A summary of cost estimates is shown in Table 4.

Table 4. Capital requirements and operating costs.

	CAPITAL REQUIREMENT*		OPERATING COST** (90% OPERATING LOAD)			
PROCESS	DOLLARS	$/KW.	$/YR.	MILLS/ KW.-HR.	$/TON OF COAL	MILLS/ 10^6 BTU
Reinluft	14,217,000	17.77	5,431,000	0.857	2.45	95.8
Alkalized alumina	8,510,000	10.64	3,402,000	0.537	1.54	60.0
Catalytic oxidation	16,999,000	21.25	3,881,000	0.613	1.75	68.4

*Includes plant cost, interest during construction, and working capital.

**Includes raw materials, utilities, labor, maintenance, overhead, and capital charges of 14% of total investment but excludes by-product credit.

217. Katell, S., & Plants, K.D. (U.S. Bur. Mines, Morgantown, W. Va.) Here's what SO_2 removal costs. Hydr. Proc. 46, July 1967, p. 161-4; cf Chem. Eng. Prog. 62, Oct. 1966, p. 67-73.

Capital costs and operating costs for SO_2 removal from flue gas based on 3 different types of methods are estimated and compared. These methods are (1) Alkalized alumina process (U.S. Bur. Mines); (2) Reinluft active carbon adsorption process (Johswich's process, West Germany) and (3) Catalytic oxidation process (such as the Monsanto Co's process). (For numerical data see abstract under ref. 216).

218. Kettner, H. (Inst. for Water-Ground and Air-Hygiene, Dusseldorf, Germany.) The removal of sulfur dioxide from flue gases. Bul. of the World Health Org. (N.Y.) 32, 421-429 (1965).

Various processes for the removal of SO_2 from flue gases are briefly described. Among them there is the wet catalytic process developed by Pauling at Esso Co. in Hamburg, Germany and adopted by Lurgi AG of Frankfurt under the trade name "Sulfacid" process. The process uses a fixed bed of carbon-containing catalyst; H_2SO_4 forms directly on the catalyst and falls off and is concentrated by the incoming gas to a 75% H_2SO_4.

219. Monkhouse, A.C., & Newall, H.E. (Dept. Sc. & Ind. Research, East Greenwich, England). Industrial gases-Recovery of sulfur dioxide. Proc. Disposal of Industrial Waste Conf., Sheffield Univ., England, 1956, p. 103-6 (Chemico reprint 2693).

The following processes of SO_2 removal from waste gases are briefly described: (1) absorption in dimethylaniline, (2) sulphidine process, (3) absorption in basic aluminum sulfate, (4) absorption in NH_4SO_3 solution, (5) scrubbing with water (6) scrubbing with aq. solns. of organic bases, (7) absorption in aq. solns. of inorganic bases, (8) Magnesium oxide processes, (9) Zinc oxide process, and (10) Lime and dolomite injection processes.

220. Slack, A.V. (T.V.A.) Air pollutions the control of SO_2 from power stacks. III. Processes of recovering $S0_2$. Chem. Eng. 74, Dec. 4, 1967, p. 188-196.

Burning coal contg. 3.5% S in a 1,000,000 kw power plant gives off 1.7 to 2.0 million SCF of flue gas per min., which contains 0.2 to 0.25% $S0_2$. The gas velocity is usually maintained at 35-50 miles per h. This makes $S0_2$ recovery costly in equipment. The wet type of processes of recovery of $S0_2$ requires cooling of the flue gas to below 300°F. which is a desired temp. to give the flue gas proper buoyancy at the top of the stack. The problem of reheating the gas, after $S0_2$ removal, if reheating is desired, adds more cost to the recovery system.

221. Bienstock, D., & Murphy, E.M. The Chemistry of sulfur dioxide. U.S. Bur. Mines, Div. of Solid Fuel Technol., Interim Report 1956, 58 pp.

The problem of air pollution by SO_2 emissions from burning coal containing S, from smelters and from H_2SO_4 plants is discussed. Plans for finding a solution to this problem are under way at U.S. Bur. of Mines in cooperation with U.S. Public Health Service. A survey of literature has been made for information useful in this project. An annotated bibliography of 84 references is presented.

222. Bienstock, D., Brunn, L.W., Murphy, E.M., & Benson, H.E. Sulfur dioxide, its chemistry and removal from industrial waste gases. U.S. Bur. Mines, Inf. Circ. 7836, 1958, 96 pp.

Phys. and chem. properties of SO_2 are reviewed. Methods of removal of SO_2 from waste gases have been investigated. Their advantages and disadvantages are discussed. 253 references.

223. Cooper, A.G. (U.S. Public Health Service Div. of Air Pollution, Washington, D.C.) Sulfur oxides and other sulfur compounds. U.S. Publication No. 1093, Bibliography Ser. No. 56, 1965, 383 pp.

A bibliography with abstracts of 994 references, 1893-1964 with subject headings and author index.

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Chemical Construction Corporation
CONSULTING DIVISION

A BIBLIOGRAPHY OF SULFUR TRIOXIDE AND SULFURIC ACID MIST EMISSIONS AND THEIR CONTROL, 1907-1968, WITH ABSTRACTS

TABLE OF CONTENTS

(Subject Index)

I. Sulfuric acid mist formation (1 to 5)

II. Physical behavior of H_2SO_4 mists (1, 6 to 16)

III. Sulfuric acid mist emissions and their control (17 to 20, 61)

IV. Mist removal in general:
  a) Filter mats (21, 22)
  b) Filter cartridges (23)
  c) Glass fiber mats (24, 25, 26)
  d) Sieve tray columns (27)
  e) Venturi scrubbers (28)
  f) Wire mesh filters (29 to 33)

V. Sulfuric acid mist removal:
  a) Review of processes (34, 35, 36)
  b) Scrubbing with alkaline solutions (37)
  c) Scrubbing with water foam (38)
  d) Ceramic filters (36, 39 to 44)
  e) Coke-bed filters (45, 46)
  f) Electrostatic precipitators (45, 47 to 50)
  g) Glass fiber mats (36, 51 to 57)
  h) Metal granules (58)
  i) Packed columns (36, 59, 60)
  j) Sonic vibrations (61, 62, 63)

Table of Contents - Page 2.

k) Steam injection and condensation (64, 65, 66)
l) Sulfuric acid solutions (67)
m) Synthetic fiber mats (68 to 75, 83)
n) Vane-type baffles (36)
o) Venturi scrubbers (76 to 79)
p) Water spray (80, 81)
q) Wire mesh filters (36, 82, 83)

VI. Sulfur trioxide removal:
a) Absorption in concentrated sulfuric acid (84, 85, 86)
b) Ammonia injection (87, 88)
c) Limestone injection (89)
d) Magnesia slurry (90)
e) Peroxysulfuric acid (91, 92)
f) Reaction with iron oxides (93. 94, 95)
g) Reduction with carbon (93, 94, 96 to 99)
h) Reduction with H_2S and CH_4 (100)
i) Steam injection and condensation (101)
j) Zinc oxide slurry (102)

VII. Analytical methods (103, 104, 105)

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A BIBLIOGRAPHY OF SULFUR TRIOXIDE AND SULFURIC ACID MIST EMISSIONS AND THEIR CONTROL, 1907-1968, WITH ABSTRACTS

1. Dooley, A., & Goodeve, C. F. (Univ. College, London, England), on sulfuric acid mist. Trans. Faraday Soc. 32, 1209-1218 (1936); C. A. 30, 7244 (3) (1936).

When SO_3 in a dry air stream is passed through water, it is not appreciably absorbed, but is converted into a H_2SO_4 mist which is stable to acids and alkalis. On the other hand when dry SO_3 vapor is passed through a 98% H_2SO_4, it is practically completely absorbed. Exptl. results indicated that good absorption of SO_3 vapor in an aq. H_2SO_4 requires an extremely low water vapor pressure. But removal of H_2SO_4 mist by absorption requires a saturated or supersaturated water pressure. Therefore, if the scrubbing liquid in a column changes continuously from 98% H_2SO_4 to pure water, the H_2SO_4 mist will pass through a maximum.

2. Gillespie, G. R., & Johnstone, H. F. (Univ. of Ill.) Particle-size distribution in some hygroscopic aerosols. Chem. Eng. Prog. 51, No. 2, 74F-80F (1955).

The formation of mist and the particle size distribution in the mist have been studied in the case of H_2SO_4, H_3PO_4, HCl, HBr and $ClSO_3H$. It was demonstrated that for a given concn. of the vapor, the substance with lowest equilibrium pressure has its critical supersaturation exceeded most, and therefore a greater number of smaller particles in the mist. It is also shown that particle size of the hygroscopic aerosols depends primarily on the manner of formation. If the hygroscopic vapor reacts with water vapor with release of considerable energy, the particle size of the aerosol is small, i.e., less than 2 microns. Examples are SO_3 in humid air forming H_2SO_4 aerosols and P_2O_5 vapor in humid air forming H_3PO_4. On the other hand, if the vapor simply condenses and then absorbs moisture without releasing a large amount of energy, the particle size will be large, i.e., 2-6 microns. Examples of the latter case are the condensation of H_2SO_4 vapor, HCl, and HBr. The problem of nucleation in the formation of aerosol has been studied. Exptl. results indicated that the addition of foreign nuclei to the air stream generally decreases particle size and increases particle number with two exceptions: (1) In the case of H_2SO_4 mist formed from SO_3 and water vapor, the introduction of additional nuclei did not affect the particle size. (2) In the case of HCl mists selfnucleation did not take place nor did the introduction of foreign nuclei have any effect until sufficient water vapor was present to dissolve the salt used as a source of nuclei. This indicates that, in this case, solid foreign particles do not act as nuclei, but when dissolved in water, the droplets absorb HCl to form an aerosol.

3. Goodeve, C.F., Eastman, A.S., & Dooley, A. The reaction between sulfur trioxide and water vapors and a new periodic phenomenon. Trans. Faraday Soc. 30, 1127-1133 (1934); C.A. 29, 2428 (6) (1935)

   The reaction between SO_3 and H_2O is very fast. Under certain conditions the H_2SO_4 mist forms periodically. Trimolecular collisions are apparently necessary. The molecules of the inert carrying gas acting as third bodies.

4. Petryanov, I.V., & Tunitskii, N.N. Formation of aerosols during the condensations of supersaturated vapors. Zh. Fiz. Khim. 13, 1131-1140 (1939); C.A. 34, 4636 (1) (1940).

   Sulfuric acid fogs were produced by mixing streams of SO_3 and H_2O vapors in capillary tubes, and their properties were detd. by means of an electrometric method. Data are given on the size and concn. of the fog droplets obtained as a function of the concn. and rate of flow of the SO_2 and H_2O streams, the temp., and the size and length of the capillary tubes. For stearic acid fogs produced by diln. with a cold gas, a diam. of about 7×10^{-6} cm. is obtained at temps. up to 187°, above 200° the diam. increases.

5. Walker, W.H., Lewis, W.K., & McAdams, W.H. Principles of chemical engineering, 3rd ed., McGraw-Hill Book Co., New York, 1937, p. 39.

   The explanation of the difficulty of absorbing sulphur trioxide made in the contact process: "If one attempts to dissolve the trioxide in water or dilute sulphuric acid, the trioxide vapor first comes in contact not with the liquid but with the water vapor which has evaporated from the liquid into the gas. It reacts with this vapor, producing minute droplets of sulphuric acid in the form of a fog, and these droplets are effectively insulated from the absorbing liquid by the gas film. One must therefore use as an absorbent a liquid, the water-vapor pressure of which is negligible, i.e., strong sulphuric acid. This is the reason why for absorption one must use acid between 97 and 98 per cent. If more dilute, the pressure of water vapor is sufficient to produce a fog, if more concentrated the partial pressure of SO_3 over it is great enough to prevent complete absorption."

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6. Amerlin, A.G., & Yashke, E.V. Dispersity of mist formed during vapor condensation on a surface. Kolloidn. Zh. 25, 3-8 (1963); C.A. 59, 51 e (1963).

   Wt.-concn. and dispersity of H_2SO_4 mist droplets condensed at the inner surface of an outside-cooled tube carrying H_2SO_4 vapor-air mixt. was detd. as function of condensation temp. and flow rate, by the ultramicroscopic method. On increase in temp. and decrease in flow rate, the size of droplets increases. Exptl. results agree quant. with previously (ibid. 24, 374(1962)) given calcns.

7. Gillespie, G. R. Particle-size distribution in hygroscopic aerosols. VI. Test on industrial sulfuric acid mist. Northwestern Univ., Doctor's dissertation, 1953, 103 pp; Diss. Abst. 13, 1125-6 (1953).

p. 39. The particle size of the H_2SO_4 mist from the tail gas of a contact plant of Am. Cyanamid Co. in Hamilton, O. was measured. The mist particles ranged from 0.6 to 3.3 microns with a mean diam. of 2.4 microns. These particles due to their relatively large size are readily recovered by a venturi-type scrubber using water as the absorbent.

8. Remy, H. Absorption of fogs appearing in chemical reactions. Z. Elektrochem. 28, 467-9 (1922); C.A. 17, 661 (2) (1923).

Chemical fogs such as SO_3 and NH_4Cl may be differentiated as dry fogs and wet fogs. The dry fogs consist of colloidal particles about 10^{-5} cm. in diam., and may be absorbed in conc. salt solns. When the dry fog is contacted with moisture, it forms wet fog. Wet fogs consist of particles about 10^{-4} cm. in diam., and best absorbed by water.

9. Remy, H. The absorption of chemical mist. Z. anorg. Chem. 39, 147-150 (1926); C.A. 20, 1289 (1) (1926).

Chemical mist consists of either dry or wet particles. The dry particles are of the order of size of colloidal particles, while the wet particles are larger. These particles do not behave like gas molecules but are more stagnant in the gas stream so that when the gas stream is contacted with a liquid absorber or a scrubbing fluid, the chances of absorption or wetting are much less than the molecules of a true gas, and the less the larger the particle. Expts. confirmed this hypothesis. On the other hand, if a filter made of paper, asbestos, or cotton is used, the larger the particles the easier they are removed from the gas stream. Electrostatic pptn. is most efficient in removing the chemical mists.

10. Remy, H. The chemistry of colloids and dusts. I-II. Chem.-Ztg. 52, 677-9, 698-9 (1928); C.A. 22, 4304 (8) (1928).

Expts. showed that conc. H_2SO_4 removes H_2SO_4 mist but not all SO_3 from a gas stream contg. the two. H_2SO_4 mist is not absorbed when the gas contg. it passes through an aq. soln. of KOH. In the gas stream from a contact H_2SO_4 plant there is cloud of dry SO_3 dust which is distinct in properties from the wet H_2SO_4 mist. Results of measurements indicate that the wet particles are larger than the upper limit of colloided particles while the dry particles are smaller. Viscosity of the absorbing liquid has adverse effect upon the percentage of SO_3 absorbed. Example: aq. solns. contg. 0.0, 0.1, 0.5 and 1.0% gelatin showed absorptive power for SO_3 of 37.4, 29.5, 22.3 and 5.1%, resp. However, wetting by water spray or steam makes the dry SO_3 particles much larger and above the colloidal-partical range. These enlarged particles form a mist. Although the mist is not absorbed upon passing through pure water, it can be absorbed by passing it through strong solutions of NH_4Cl or $CaCl_2$, or absorbed on gas-mask carbon on filter paper, because the particles in the mist are sufficiently large.

11. Remy, H. & Behre, C. The absorption of fogs blown out of fuming sulfuric acid. Kolloid-Z. 71, 129-145 (1935); C.A. 29, 7741 (9) (1935).

The absorption of fogs satd. with moisture bears no simple relation to the concn. of free SO_3 in the acid used, being nearly const. in the range 25-35% SO_3, passing through a very sharp min. at about 40% SO_3, and increasing with further increase in SO_3 content. The absorption of fogs from acid contg. less than 35% SO_3 is higher than that of fogs with the same SO_3 content prepd. from acid contg. more than 35% SO_3. Expts. in which the fogs were dild. with air show that absorption is independent of the SO_3 concn. of the fog, but decreases linearly with increasing rate of flow. Liquids of low viscosity and low surface tension appear to be the best absorbents.

12. Remy, H., & Koch, C. The fogs occurring in chemical reactions. III. Examination of chemical fogs for electrical charges. Z. anorg. allg. Chem. 139, 69-80 (1924); C.A. 19, 595 (8) (1925).

Carefully dried SO_3 and NH_4Cl fogs were examd. by lead and quadrant electrometers but no charged particles could be detected. On passage through a strong elec. field no deflection of the illuminated fogs could be seen. After bubbling through H_2O, such charges could be demonstrated, as was found also to be the case with H and air.

13. Remy, H., & Seemann, W. The effect of bubble size on the absorption of fogs by liquids. Kolloid-Z. 72, 5-12, 279-291 (1935); C.A. 29, 7742 (23) (1935).

The absorption of H_2SO_4 mist by a liquid is decreased as the size of the bubble of the gas contg. the mist is increased.

14. Remy, H. & Vick, E. Absorption of chemical fogs in gas wash bottles. Kolloid-Z. 68, 22-29 (1934); C.A. 28, 6358 (a) (1934).

The absorption of damp NH_4Cl and SO_3 fogs, having opposite heats of soln., was tested with H_2O, 96% EtOH and 1% aq. gelatin soln. covered with ether, in Drechsel, Volhard, Winkler and Jena 83G1 fritted glass filter gas wash bottles. The tests were at room temp., 14.5-22.3°, with gas flow of 0.2 l./min., data were taken in each expt. for 6 mins. The best results, 98% or better absorption, were in the bottles with the fritted glass filter. There was little difference in the efficiency of the absorbing liquids.

15. Schytil, F. Absorption of sulfuric acid fumes. Ang. Chem. 62, 459 (1950); Absd. by Ind. Chemist (London) 27, 229 (May 1951).

Absorption of H_2SO_4 fumes (droplets of 0.5-3 micron diam.) depends on the water vapor pressures of both the fume droplets and the absorbent liq. which is usually a H_2SO_4 of certain concentration. The temp of the fume and that of the absorbent liq. is also an important factor.

16. Tikhomirov, M.V., Tunitskii, N.N., & Petryanov, I.V. The influence of van der Walls forces on coagulation of aerosols. Acta Physicochim. U.S.S.R. 17, 185-196 (1942) (in English); C.A. 37, 4609 (3) (1943).

The equation for the rate of coagulation of H_2SO_4 mist is derived from the radius of the particle, temp. and a coagulation constant which includes a factor γ. γ is independent of the particle size, but is determined by the constants of the van der Walls forces. The γ factor and the rate of coagulation have been determined for 3 mists: mineral oil, tritolyl phosphate, and H_2SO_4. Data are given.

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17. Amelin, A.G. and Borodastova, S.B. The mechanism of mist formation during the concentration of sulfuric acid. Zh. Prikl. Khim. 29, 721-7 (1956). (Chemico transl. TR-143.)

In a multistage H_2SO_4 concentrator using combustion gases as the heat source, the amount of H_2SO_4 mist in the exit gases may be decreased by using suitable equipment and operating conditions that ensure surface condensation of the H_2SO_4 vapor. If the gas temp. is increased between stages, and if the hot combustion gas is supplied through a separate nozzle, the degree of vapor supersaturation will be decreased and the amount of H_2SO_4 mist diminished. When superheated steam is used as a heat source, the H_2SO_4 vapor supersaturation is less than when combustion gases are used, because the dimensionless coeff. delta in the equation for degree of supersaturation is twice as large in steam as in air.

18. Berger, J.H., & Gloster, A.J. (Chem. Construction Corp., New York, N.Y.) "Chemico" drum-type sulfuric acid concentrator. Chem. Eng. Prog. 43, 225-236 (May 1947).

The H_2SO_4 mist emissions from drum-type concentrators, using combustion gases as the heat source, may be reduced to a minimum by carefully controlling the acid strength in the 2nd-stage drum so that it is always within narrow limits (e.g. 68-71% at the feed point and 93-96% at the discharge point of that stage) and by regulating the auxiliary combustion gas stream so that the acid temp. is also within narrow limits (e.g. 340-360°F). In this arrangement the 1st-stage drum serves mainly as a cooler for the combustion gases from the 2nd-stage drum on its way to the electrostatic precipitator where the H_2SO_4 mist is removed. The capacity of the electrostatic precipitator is selected to match the amount of mist to be cont'd 18. removed. In an example where the acid is concentrated in the 2nd-stage drum from 68 to 93% H_2SO_4, the mist content in the combustion gases entering the electrostatic precipitator is in the range of 240-340 mg/cu.ft. (approx. 0.6-1.16% by wt.).

19. Gillespie, G.R. & Johnstone, H.F. Particle-size distribution in some hygroscopic aerosols. Chem. Eng. Prog. 51, 74-80 (Feb. 1955).

    Samples of tail gases from a commercial contact H_2SO_4 plant were taken at a point about 3 feet above the absorption column. The SO_3 mist loading was found to be 0.62-0.73 mg./l., resp. (corresponding to 495 and 583 ppm.; resp., by wt.). The sizes of the particles of the H_2SO_4 mist ranged from 0.2 to 1.5 microns, and the size distribution was of the same pattern as that of mists made in the laboratory made of SO_3 and humid air. The particles of the mist grow in size with time.

20. U.S. Public Health Service. Atmospheric emissions from sulfuric acid manufacturing processes. U.S. Public Health Service, Environmental Health Services, Air Pollution. Publication No. 999-AP-13, 1965, 127 pp. U.S. Govt. Printing Office, Washington D.C., $0.60; Chemico reprint 2908.

    U.S. has about 163 contact H_2SO_4 plants and about 60 chamber H_2SO_4 plants. The primary emissions from the chamber plants contain SO_2 0.1-0.2%, N oxides (mostly NO_2) 0.1-0.2%, and H_2SO_4 mist 5-30 mg./scf. 90% of the mist is larger than 3 microns in diameter. Equipment for reducing the emissions beyond the Gay Lussac tower is rarely employed. Emissions from the contact plants contain SO_2 0.1-0.5%, SO_3 0.5 to 48 mg./scf., and H_2SO_4 mist 3-15 mg./scf. Electrostatic precipitators, glass-fiber mat or stainless steel wire mesh pads eliminate 94-99.9% of the mist, but do not remove SO_2 or dry SO_3. Some plants use the Cominco process to reduce the SO_2 content in the tail gas to about 0.03% in 2-stages of NH_4HSO_3 scrubbing. But, Cominco process does not remove H_2SO_4 mist.

21. Carmichael, Jr., L. and Reese, A. Apparatus for Removing Liquid Particles in a Gas Stream. U.S. Pat. 3 339 351 (Cl. 55-350), Sept. 5, 1967, (appl. March 12, 1965).

    Mists with particle size in the range 0.25 to 10 microns are removed from gas streams by a 2-stage "agglomeration filter" made of mats of fine fibers (0.0003-0.15 inch diam.). The first-stage mat is 0.1-0.5 inch thick with 50-80% void. The second-stage mat is 4-6 inches thick with 97-99% void.

22. Plaut, W., & Fairs, G.L. (to Imp. Chem. Inds. Ltd.). Fiber filters for the removal of fine mists. U.S. Pat 3 107 986 (Cl. 55-97) Oct. 22, 1963 (appl. in Britain Nov. 28, 1956).

cont'd 22. Mists comprising aq. particles less than 5 microns in diam. are removed by a mat of non-wettable fibers which range in diam. from 5 microns to 50 microns and which are neither woven nor felted. The mats contain 80 to 98% voids. The mist would collect on the fibers in the form of discreet droplets.

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23. Fulford, E.H., & Searcy, J.E., Jr. (to Fram Corporation, Providence, R.I.) Gas separator/filter apparatus. U.S. Pat. 3 201 924 (Cl. 55-324) Aug. 24, 1965 (appl. July 24, 1962).

The mist remover is made in cartridges of fibrous material. Gases carrying mists pass from the outside to the inside of the cartridge and out through its top. Liquid drops follow down from the inner surface into a sump.

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24. Anon.-1956. Remove liquid entrainment better. Chem. Eng. 63, No. 2, 230 (1956).

The wire-mesh mist remover is manufactured by Metal Textile Corp., Roselle, N.J. For liquid particles mostly 5 microns or larger a single mat of multilayered knitted metal wire mesh will do. For liquid particles in the submicron range, an extra mat is necessary to serve as a preliminary step. This extra mat is made of layers of glass fibers and metal wire knitted together in parallel. The glass fibers seem to cause the fog to coalesce. After that the droplets of increased size are caught by the second stage mat of all-metal wire mesh. These mats give high efficiency at low pressure drop.

25. Baker, C.O., & Scauzillo, F.R. (to Socony Mobile Oil Co.) Mist extractor. U.S. Pat. 3 010 537, Nov. 28, 1961.

A glass-wool mat is used to remove mists from gases.

26. Blasewitz, A.G., & Judson, B.F. Filtration of radio active aerosols by glass fibers. Chem. Eng. Prog. 51, 6-11 (Jan. 1955).

Satisfactory performance over periods of 1-3 years have been recorded with air filters made of glass fiber mats at the Hanford Atomic Products Operation. The filter units range in sizes from 200 to 20,000 cu. ft./min. The collection efficiency of these units is about 99.99% when operated with gases contg. varying amounts of submicron particles and acid vapors; the latter often as high as 50% by volume. (The glass fibers can be operated at a temp. as high as 500°F.) The pressure drop of the glass fiber filters was studied at superficial velocity of 5-100 ft./min. The pressure drop is generally low (2.2-4.0 inches water). Data are presented in terms of x, y, z, the exponents of the equation $\Delta p = KL^x p_p^y V^z$, and u. Where K = a constant; L = bed depth; p_p = packing density; V = superficial velocity; and u = fiber diam. The glass fiber air filters installed at Hanford are expected to last for at least 15 years without developing excessive back pressures.

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27. Sze, M.C. (to Hydrocarbon Research Inc.) Mist removal from gases. U.S. Pat. 2 801 709, Aug. 6, 1957.

A mist collector is specified in which the gas velocity increased progressively as the gas passes from one stage to the next, each stage having a sieve plate with holes facing an impact surface while the liquid resulting from coalescence flowing by gravity to the collecting channels.

28. Harris, L.S. (Schutte and Koerting Co., Cornwells Heights, Pa.) Fume scrubbing with the ejector Venturi system. Chem. Eng. Prog. 62, Apr. 1966, p. 55 59; C.A. 65, 341 d (1966).

Mist and dust particles smaller than 2 microns in diameter are effectively removed from gas streams by scrubbing with an ejector Venturi scrubber. The scrubber also acts as a suction pump so the gas under treatment may flow at a desired rate without using a blower. For submicron particles in the gas the ejector Venturi scrubber could be made with two-stages. The collection efficiency increases with the liquid (water or alkaline solution) to gas volume ratio, L/G; and for a constant L/G, it increases with the motive pressure of the liquid supply.

29. Campbell, J.A. Gas & Liquid Separator. U.S. Pat. 2 511 967. June 20, 1950.

The apparatus comprises a vertical cylindrical tank with a gas inlet tube attached tangentially about the middle of the tank. Inside of the tank the cylindrical baffle plate and the gas outlet tube are arranged in a coaxial manner attached at the top of the tank with the outlet tube protruding. There is a liquid outlet at the bottom of the tank. Under operating conditions a certain amount of liquid is retained at the bottom of the tank with the liquid level high enough to seal off the bottom opening of the baffle plate but not high enough to reach the outlet tube. The flow of gas is directed along the inner surface of the tank; at a point more than 180° away from the inlet tube, the gas passes through a vertical slot at the top of the baffle plate into an inner chamber which is formed by the baffle plate and the outlet tube. The bottom of the outlet tube is closed by a plate, but there are vertical slots in that part of the outlet tube surrounded by the baffle plate. The same part is wrapped around by multiple layer of wire-cloth. A layer of wire-cloth is also provided along the inner surface set about 1/4" away from it.

30. Fisher, J.P., & Downs, G.F. (to Empire Oil & Ref. Co.) Apparatus for cleaning gas. U.S. Pat 1 824 713, Sept. 22, 1931.

A cylindrical vessel is specified into which the gas carrying entrainment is passed through a ring of nozzles located around the lower part of the vessel so as to impart a whirling movement to the gas as it passes up the cylindrical vessel. In the upper part of the vessel hanging down from the centrally cont'd30. located outlet tube is a cartridge of filtering screen through which the gas finally passes on its way to the outlet. By using this apparatus the larger droplets in the gas stream would be thrown against the inner surface of the vessel and then fall down into a liquid reservoir below; and the smaller droplets would adhere to the filtering screen and coalesce and then drop off into the liquid reservoir which is maintained at a constant level by a drain pipe with a trap.

31. Neeson, C.R. (to Chrysler Corp.) Gas and liquid separator. U.S. Pat. 2 510 049, May 30, 1950.

The apparatus comprises a vertical cylindrical shell with a cartridge of wire gauze fixed against the upper end of the shell where the gas outlet is located. The inlet tube is located a little way from the top; said tube protrudes inside the shell with the inside opening sealed off but a slot is cut to permit gas to enter the apparatus horizontally and tengential to the inside surface of the shell. There is a diaphragm which seals off the annular space at the lower end of the said cartridge, so that all gas passes through the gauze to the outlet nozzle. The lower part of the shell, that is, below the diaphragm contains a reservoir for the liquid and a constant level device connected with the discharge valve for the liquid.

32. Reynolds, S.C. (Metal Textile Corp. Roselle, N.J.) Entrainment eliminators save money. Petr. Ref. 32, No. 7, 138-140 (1953).

The device that removes liquid entrainment from vapors and gases is knitted wire-mesh mat 4-8 inch thick that permits one to see light through it and yet stops better than 99% of the entrainment of a particle size down to 1 micron. The mat made of steel, Monel, or 18-8 stainless steel wire (e.g., 0.011 inch in diam.) has free volume of 98%, and a surface area of 125 sq. ft. per cu ft. The mat in 18-8 stainless steel costs \$9.-\$10 per sq. ft., 4 inches thick. That in plain steel costs 1/4 as much. In operation there is a range of optimum vapor or gas velocity to be used which is high enough to cause impingement of the droplets and prevent them from drifting through the mat, and yet not too high as to sweep the coalesced drops from the mat into the down-stream vapor or gas. With air-water system at atmospheric pressure, the optimum velocity range was found to be 2-12 ft./sec. In vacuum the upper limit would be increased, while under pressure it would be reduced. Due to its open structure, the resistance to gas flow is very low, e.g., not over 1 inch of water.

33. York, O.H. Performance of wire-mesh demisters. Chem. Eng. Prog. 50, 421-4 (Aug. 1954); C.A. 48, 11122 h (1954).

The wire-mesh type of entrainment remover as applied to distillation columns is described. The wire-mesh most commonly used is a knitted mat made of 0.011-inch wire of Monel or other metal with a bulk density ont'd 33. of approx. 12 lb/cu. ft. and a surface area of 110 sq. ft. /cu. ft. The efficiency of entrainment removal for a 4-inch thick mat is 99.9 wt. % over a wide range of vapor or gas velocities, e.g., 3-13 ft. per sec. The pressure drop is rarely more than 1 inch of water. By suitable arrangement an effluent may contain as low as one part of liquid per 10 billion parts of gas or vapor by weight. The cost of wire-mesh mats including the supporting grids is estimated for a typical installation: total capacity 50,000 cu. ft. /min., wire mesh made of 18-8 stainless steel or Monel metal; approx. $24.00/(100 cu. ft.) (min.).

34. Fair, G.L. Removal of acid mist. J. Soc. Chem. Ind. 60, 141-6 (1941); C.A. 35, 7661 (8) (1941).

H_2SO_4 mist produced during the manufacture of the acid is commonly removed from the tail gas by 3 methods: (1) The packed scrubber, eg., the coke filter; the removal is satisfactory, but its bulkiness makes it unpopular. (2) The centrifugal separator; it removes particles down to 2 microns in diam.: scrubbing efficiency is about 97%. (3) The electrostatic precipitator; it removes particles all sizes, and gives a scrubbing efficiency of 99.9%.

35. Kerrigan, J.V., Snajberk, K., & Anderson, E.S. (Univ. of California, Richmond). Collection of sulfuric acid mist in the presence of a higher sulfur dioxide background. Anal. Chem. 32, 1168-1171 (1960); C.A. 54, 23449 b (1960).

The electrostatic precipitator, the Greenburg-Smith impinger, and the sintered-glass filter are evaluated as to their efficiency in collecting H_2SO_4 mist when a higher SO_2 background is present. The results show that these instruments yield reproducible results over the concn. range of 0.5-150 mg. H_2SO_4 mist/cu. m., and are efficient at low and high concns. This study establishes the ability of these instruments to collect H_2SO_4 mist accurately at concns. found in the atm. under field conditions.

36. Massey, O.D. (Stauffer Chem. Co., Houston, Tex.) Demister for sulfuric acid plant stacks. Paper presented at Air and Water Pollution Abatement Conference, M.C.A., Cincinnati, O., March 1959; abst. in Chem. Eng. 66, July 13, 1959, p. 143-6; Chem. Eng. Prog. 55, May 1959, p. 114-8; Sulphur (London) Sp. issue 1959, p. 16-19; C.A. 53, 14608 h (1959).

Using a 2-stage wire-mesh demister unit on the tail gas of a 98% H_2SO_4 plant, a tenfold reduction of acid mist was obtained at pressure drop of 1.5-2.0 inches of water. This corresponds to a H_2SO_4 content of 1-2 mg. /cu. ft. in the stack gas, and the stack plumes were practically invisible. However the wire-mesh demister unit, even with a 3rd stage, was found ineffective when used on the tail gas of an oleum plant.

cont'd 36. Other mist removers, which were less efficient than the knitted wire mesh, were also tested. They were (1) packed beds of Berl saddles, (2) vane-type baffles, and (3) Lurgi filters (porous ceramic thimbles). Performance data of these and the knitted wire mesh demister are given as follows:

Comparative Filter Performance Data

Pressure Drop, In. H_2O	Mg. H_2SO_4/Cu. Ft. Inlet	Mg. H_2SO_4/Cu. Ft. Outlet	Efficiency, %
Packed Bed, 12-In. Layer of 1-In. Berl Saddles—Table I (Velocity: 7, 10, 12 and 20 ft./sec.)			
⅜	16.5	14.5	12
¾	18.3	6.4	65
1¼	25.8	11.6	55
3¼	46.7	28.8	38*
Vane Filter, Face Velocity about 30 Ft./Sec.—Table II			
2¼	34.8	16.9	51.4
2	14.2	6.8	51.8
2	28.6	5.2	81.8
2	35.2	3.3	90.6
Vane Filter, Face Velocity About 50 Ft./Sec.—Table III			
4	26.3	2.3	91.4
4	18.8	4.1	78.2
Lurgi Filter, Velocity About 5 Ft./Sec.*—Table IV			
9	15.8	1.5	90.5
10	59.6	2.8	95.3
10	54.9	0.8	98.6
8	21.4	6.0	72.0
8	17.5	4.5	75.0
Wire-Mesh Filter, 2-Stage, Velocity 12 to 15 Ft./Sec.—Table V			
1	8.8	0.70	92.5
¾	4.1	0.74	82.0
1¼	13.8	0.92	93.4
1¼	66.9	0.77	98.9
1½	32.5	0.98	97.0
1½	13.0	0.76	94.1

* Re-entrainment probably occuring

* Filter tube sheet area of 116 sq. ft.

Knitted Wire-Mesh Filter Specifications†—Table VI

Density, Lb./Cu. Ft.	Surface Area, Sq. Ft./Cu. Ft.	Free Volume, Approx. %	Thickness,* In.
14	120	96	4
12	115	97	4
9	85	98	4, 6
7	65	99	6
5	45	99	6

*Thickness varies with efficiency desired and allowable pressure drop.

† Wire sizes available from 0.003 to 0.016 in. Usually 0.011 in. used; above data for 0.011 in.

37. Alekseeva, M.V., & Andronov, B.E. Absorption of sulfuric acid fog. Lab. Prakt. (U.S.S.R.) 16, No. 1, 8-21(1941); C.A. 35, 4921 (7) (1941).

H_2SO_4 and HNO_3 fogs completely absorbed by an aq. soln. of 0.02 N alkali placed in a train of 5 wash-bottles in series with gas velocity 0.25-0.5 l./min. and pressure drop of 130 mm. Hg. The gas stream passes a fritted glass filter in the 3rd-stage wash bottle.

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38. Btansky, D.W., & Diwory, D.J. Removal of sulfuric acid fog by bubble phase absorption. Nat'. Petr. News 32, No. 22, R-200-1; Refiner Natural Gasoline Mfr. 19, 191-5 (1940); C.A. 34, 6054 (2) (1940); Proc. Am. Petr. Inst. 10th mid-yr. meeting, 21, 39-45 (1940).

The gas contg. H_2SO_4 fog is scrubbed with a soln. of a petroleum sulfonic acid, which forms a foam and catches 93-95% of the H_2SO_4 fog in 10-11 sec.

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39. Anon.-1960. Ceramic filter for acid mist. Brit. Chem. Eng. 5, June 1960, p. 400.

The Lurgi ceramic filter for H_2SO_4 is a bundle of tubes through which the pores are of a specially designed size and number. In operation gas enters the tubes placed at the base of the stack before an induced draft fan. The H_2SO_4 mist coalesces in the pores and flows down as a liquid stream on the outside of the tubes where it is collected and recovered. The clean gas passes through the tube wall and out into the stack.

40. Edeleanu G.m.b.H. Removing sulfur trioxide mist from gases. German Pat. 549 342, Feb. 4, 1928; C.A. 26, 3860 (4) (1932).

The gas contg. SO_3 mist is passed through a filter made of mineral material which is kept moist.

41. Fletcher, A.W. (Fuel Research Station, London, England.) Determination of sulfur trioxide in gases. The efficiency of a sintered-glass filter in recovering sulfuric acid mist. Chem. & Ind. 1954, 777-8; C.A. 48, 11244 d (1954).

Gaseous mixt. contg. 0.0002-0.004% SO_3 as H_2SO_4 mist were analyzed for SO_3 by the Corbett method (J. Inst. Fuel 24, 247-251 (1951); C.A. 46, 237 i (1952). The results showed a high efficiency of collection of H_2SO_4 mixt. on the "Grade 4" sintered-glass filter.

42. Leonard, C.L., Schneider, C.R., & Sheppard, J.K. (to Union Carbide Corp.) Sulfuric acid mist removal. U.S. Pat. 2 906 372, Sept. 29, 1959; C.A. 54, 988 b (1960).

Gas streams contg. H_2SO_4 mist are passed through a plate of porous SiO_2 which is continuously wetted by 60-72% H_2SO_4 at 110°-130° to remove the H_2SO_4 mist from the gas stream.

43. Markward, H.G. The removal of sulfuric acid mist. Ind. Chemist 36, 220-2 (May 1960).

The operating data of the Lurgi ceramic filter tubes for the removal of H_2SO_4 mist are given. When the pressure drop across the filter is properly adjusted the amount of mist in the gas stream is decreased from 0.34-0.589 to 0.002-0.20 gr. SO_3/SCF, resp. The pressure drop across the filter is 9 inches water at start and 12-13 inches towards the end of the 3rd month of operation.

44. Schytil, F., & Krollmann, H. (to Metallgesellschaft A.G.) Collecting the liquid contained in mist. U.S. Pat. 2 947 382. Aug. 2, 1960.

The H_2SO_4 mist is filtered out by a ceramic plate with pores in the range 0.2-3 microns.

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45. Anon.-1959. New installation for pollution control. Chem. Eng. Prog. 55, Mar. 1959, p. 41.

At Allied Chem. Corp's H_2SO_4 plant two batteries of electrostatic pptor. have been installed to replace a row of coke-boxes for the removal of H_2SO_4 mist. Another row of coke boxes is retained for the time being.

46. Ruibnikov, G. Effect of steam on the degree of precipitation of sulfuric acid mist. Khimstroi 7, 45-46 (1935); C.A. 29, 3200 (b) (1935).

The H_2SO_4 mist is more effectively removed by introducing steam into the gas and pass the gas through a coke filter. The amount of SO_3 removed is nearly doubled by this improvement.

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47. Perevezentsev, I.G., & Tarasova, A.A. Separating SO_3 from SO_2 during the determination of the degree of contacting in the production of contact sulfuric acid. Trudy Ural. Nauk.-Issledovatel. Khim. Inst. 1957 No. 4, 223-6; C.A. 54, 6054 b (1960).

A mixt. contg. 6-7% SO_3 and 0.2-0.4% SO_2 in air corresponding to gas mixts. at the exit of contact app. in the H_2SO_4 production is bubbled through 3-4 mm. of H_2O or dil. H_2SO_4 to form a fog of H_2SO_4. The fog is removed in a high-voltage electro-filter. This simplifies the analysis of the residual SO_2, since the gas leaving the electrofilter is entirely free of SO_3, but its SO_2 content does not change.

48. Stastny, E.P. (Koppers Co. Inc., Baltimore, Md.) Electrostatic precipitation. Chem. Eng. Prog. 62, Apr. 1966, p. 47-50.

ont'd 48. Between 85 and 95% of the H_2SO_4 mists from the oleum tower are particles smaller than 2 microns, while only about 30% of the particles from the 98% acid absorber are smaller than 2 microns. To remove H_2SO_4 mists of less than 2 microns, the ordinary wire-mesh type mist collector is not effective, but an electrostatic precipitator serves the purpose with high efficiency. At a low, but practical, gas rate through the electrostatic precipitator, the exit gas contains as low as 0.03 mg H_2SO_4 per SCF when treating gas from a 98% H_2SO_4 absorber. In one installation attached to a combination of 2 white 98% acid, 1 black 99% acid, and 1 black 104.5% oleum tower, the mist loading was 9 mg. H_2SO_4/SCF, and the stack gas had a residual mist content of 0.08 mg. H_2SO_4/SCF. The H_2SO_4 plant stack usually shows a visible plume when the residual mist is more than 0.12 mg. H_2SO_4/SCF. The N oxides, if present in the H_2SO_4 tail gas, is also eliminated by the electrostatic precipitator. The SO_2 present in the H_2SO_4 plant tail gas is mostly eliminated in the precipitator by the action of ozone produced by the corona effect on the electrodes. The ozone oxidizes SO_2 to form SO_3 and the moisture (after purposely added) converts it to H_2SO_4 mist which is removed along with the mist originally present.

49. Stopperka, K. (Tech. Univ., Dresden, Germany) Electrostatic deposition of sulfuric acid mists from waste gases of sulfuric acid manufacture. Staub (Dusseldorf) 25, 508-512 (1965) (in German); C.A. 64, 12202 c (1966).

Pilot plant investigation, using different sized plates, various humidities, and different shaped discharge electrodes are discussed. The system that gave the best results used Korobon tube electrodes (Korobon is graphite within a phenolformaldehyde matrix which proved corrosion-free after 4 months of continuous use) and the addn. of water at the rate of 15 g./m^3 (which gave a clear condensate with 25 to 55% H_2SO_4). Detailed dimensions of the lead-barbed discharge electrodes and other operating data are presented.

50. Stopperka, K., Neumann, V., & Hose, W. (Univ. Dresden, East Germany). Electrostatic separation of sulfuric acid clouds. Chem. Tech. (Berlin) 18, 321-7 (1966); Brit. Chem. Eng. II, 807 (Aug. 1966); C.A. 65, 18203 e (1966).

The electrostatic precipitator was studied in connection with the removal of SO_3 from exhaust gases of the Gips process. The SO_3 content was approx. 620 mg. per cu.m. Water was sprayed into the gas stream so that the liquid collected from the electrostatic precipitator is an approx. 50% H_2SO_4. Tests of various designs of the component showed that the tubes are better than plates as acid collectors and a twisted ribbon with up-pointing spikes is preferred as the corona electrode. The tubes are made of impregnated carbon (Korobon). Gas velocity is 1.96 m./sec. corresponding to a residence time of 2.04 sec. At a voltage of 70 kv. the removal of SO_3 was complete.

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51. Brink, J.A. (Monsanto Chem. Co.) Blocks air pollution, snares 1700 lb. of H_2SO_4 per day. Chem. Processing 25, Feb. 1962, p. 40-41.

    H_2SO_4 mist is removed by filters made of glass fibers made in the form of bags hanging from a tube-sheet. The unit consists of 22 bags or tubes 18" diam. and 8' long reinforced by resistant wire mesh. The gas volume handled was 22,000 SCF/min. at 180°F. contg. 0.3-3.0 micron H_2SO_4 particles. The pressure drop across filter was 7.25 inches of water. Removal was 99.98%. Quantity recovered was 1,700 lbs. H_2SO_4 per day.

52. Chapman, F.F. (to Canadian Inds. Ltd.) Separation of chemical mists from gases. Can. Pat. 442,210, June 17, 1956; C.A. 41, 6446 f (1947).

    H_2SO_4 mixt. is removed from gases by passing them through a fabric woven from glass fibers.

53. Fairs, G.L. (Imp.-Chem. Inds. Ltd.) High efficiency fiber filters for the treatment of fine mists. Trans. Instn. Chem. Engrs. 36, 476-485 (1958).

    H_2SO_4 mist of less than 2 microns diam. has been effectively collected by a filter pad made of silicone coated glass wool. The silicone coating renders the glass fibers water repellent and causes coalescense of the H_2SO_4 droplets, and an improvement of mist collection of 12 times. (The exit gas from uncoated glass wool contained 0.2% H_2SO_4.) Garnetted terelyne polyester fiber gave similar results as coated glass fiber, with a scrubbing efficiency of 99.6%.

54. Gille, H. The absorption of chemical clouds. Z. angew. Chem. 39, 401-2 (1926); C.A. 20, 2712 (4) (1926).

    Gas from pyrite burners, if moist, may be freed from SO_3 by passing the gas through a plug of wadding. The SO_3 thus retained may be recovered by washing the wadding. If the gas is dry the wadding retains little or no SO_3.

55. Hennig, R.R. (to Allied Chem. Corp.) Filter for removal of droplets from gas streams. U.S. Pat. 2,771,153, Nov. 20, 1956; C.A. 53, 20953 b (1959).

    Droplets of liquid, e.g. H_2SO_4, entrained in a gas stream are removed by passing the mixture through an app. contg. filter material, e.g. glass wool, permeable to gas but not to liquid. Liquid draining from the filter forms a seal at the bottom, preventing the mixt. from by-passing the filter.

56. Vashke, E.V., Amerlin, A.G., Petrovskii, V.A., & Osmulkevich, V.A. Glass wool filters for trapping sulfuric acid mist. Khim, Prom. 1965 (3) 196-200 (in Russian); C.A. 63, 1499 f (1965).

ont'd 56. Two types of filters packed with glass wool (compn. SiO_2 70.5-72.5, CaO 6.7-6.9, MgO 3.9-4.0, Na_2O 14.6-17.1, and trivalent metal oxides 1.7-2.1%) with a fiber diam. of 25 microns are described; lab. expts. showed that the glass wool resisted prolonged effect (400-600 hrs.) of 75-98% H_2SO_4, but was destroyed by more dil. acid. The hydraulic resistance (ΔH) of filters packed to a height of 100-300 mm. with glass wool increased with increasing content of H_2SO_4 mist in the gases passing through the filter and with increasing gas velocity; the degree of trapping of the mist increased with increasing ΔH and with increasing diam. (d) of the H_2SO_4 droplets in the mist, within the d range between 0.3 microns and 1.0 microns. Large-scale expts. showed that when the initial mist content in the gas was 38-60 g./m.^{3}, a degree of purification of 99.7% (i.e., a final mist content of 0.12 g./m.^{3}) was obtained by using a filter with a ΔH of 160-390 mm. Hg. Although the expenditure of elec. energy needed to transport the gas through a glass-wool-packed filter is larger than that needed for an electrostatic precipitator, the glass-wool filter is preferred because of its much lower cost and lower maintenance.

57. Wong, J.B., Ranz, W.E., & Johnstone, H.F. (Univ. of Ill.) Collection efficiency of aerosol particles and resistance to flow through fiber mats. J. Appl. Phys. 27, 161-9 (1956); C.A. 50, 11725 a (1956).

The collection efficiencies for H_2SO_4 aerosols of 0.4-1.3 microns particle diam., and the resistance to flow through glass fiber mats composed of 3.5, 6.2, and 9.6 micron fibers, were investigated. The results agree with the theory that particle collection in this range is a function of the inertia of the particles, the interception by the fibers, and the nature of the flow around the fibers, as characterized by the inertial parameter ψ, ratio of the diam. of the aerosol particles to the diam. of the fiber (interception parameter), and that the pressure drop is a function of the flow characteristics and the fiber interfering effect. Theoretical equations for collection efficiency and pressure drop of the fiber mats were analyzed in terms of the impaction efficiency and drag coefficient of single fibers. These equations were evaluated by comparing the apparent fiber efficiency and drag with theoretical values. ($\psi = S/Dc$; S = stopping distance of a particle in still gas when given initial velocity, Vo; and Dc = diam. of glass fiber.)

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58. Sté.des Forges et Chantier de la Mediterranee. Purification of combustion gases. Fr. Pat. 1 399 747 (Cl. C 01b) May 21, 1965 (appl. 10, 1964); C.A. 64, 487 c (1966).

An app. and process for the purification of gas produced by the combustion of fuel oil or coal in boilers are described, in which a heat exchanger contg. porous metal granules cools the gas below its dew point, and the granules entrain the mist of H_2SO_4 produced by the combination of SO_2 and SO_3 with condensed H_2O.

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59. Chemiebau Dr. A. Zieren GmbH. (Zieren, A., & Schuett, H., inventors). Separation of fine sulfuric acid mists. Ger. Pat. Appl. 1,217,347 (Cl. C 01b) May 26, 1966 (appl. Sept. 15, 1952); C.A. 65, 10183 e (1966).

H_2SO_4-contg. gas is passed through a thin layer of granular Pb or glass material (2-5 mm.) in spherical or other form at a rate of 1750-3700 $m.^3/hr.\ m^2$. to sep. the H_2SO_4 mixt. The sepn. unit can consist of 3 or more layers of granules or spheres. The tail gas of a H_2SO_4 chamber process was passed through a bed of the above-described SiO_2 spheres at 3150 $m^3./hr.\ m^2$. The mist content of 300 mg. was reduced to 10 $mg./m^3$. The Reynolds no. was 199. The process is useful for the sepn. of all finely divided H_2SO_4 mists which consist of liquid droplets, as they occur, for instance in the production of H_2SO_4, in the purification of SO_2-contg. gases prior to catalyst treatment, in the conversion of H_2S to H_2SO_4, etc.

60. Hartig, R.G., & Archer, J.R. (to Int'l. Min. & Chem. Corp.) Recovery of chemical mists from gases. U.S. Pat. 2,901,061, Aug. 25, 1959; C.A. 53, 22794 d (1959).

Mists of SO_3, halides, and P_2O_5 are removed from gases by passing the latter through beds of 10-30 mesh inert material while passing a liquid countercurrent to it, but in an amt. insufficient to flood the voids, and thus maintain a back pressure on the gas stream of 10-30 in. H_2O.

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61. Danser, Jr., H.W. Eliminate stack dusts and mists. Chem. Eng. 57, May 1950, p. 158-160.

A siren-type sonic generator creating a sound pressure of over 150 decibels, operates in the passage of a gas contg. H_2SO_4 mist amtg. to 300 mg of H_2SO_4 per cu. ft. The sound agglomerates the fine liq. particles which are then collected by a number of small-diam., high velocity, cyclone dust collectors operating in parallel. A normal contact H_2SO_4 plant gives a tail gas containing generally less than 60 mg. H_2SO_4 mist per cu. ft., while the tail gas leaving a drum concentrator may contain as high as 300 mg. H_2SO_4 mist per cu. ft. A sonic precipitator would reduce the mist content down to less than 5 mg./cu. ft., which would be low enough to meet the air pollution control requirements in a majority of localities.

62. Jahn, R. A new method for the separation of sulfur trioxide mist from gases containing sulfur dioxide. Papier (Darmstadt, Germany) 16, 433-4 (1962); C.A. 58, 655 h (1963).

A simpler method has been devised for the sepn. of SO_3 microparticles than that requiring electrofilters. The new technique resorts to sound waves transmitted through appropriately placed pipes. In this way, the very finely divided SO_3 particles are coagulated so that they can be removed to the extent of 99% of the SO_3 present in the mist. The new technique is also considerably cheaper than the one requiring electrofilters.

63. Nord, M. (Wayne Univ., Detroit, Mich.) Sonic precipitation of smoke fumes and dust particles. Chem. Eng. 57, Oct. 1950, p. 116-9; cf. ibid., 57, May 1950, p. 158-160.

The theory of sonic precipitation of aerosols from a gas stream is discussed. High-intensity sound waves (on the order of 160 decibels equivalent to 2 watts/sq. cm.) produce vibrations of the aerosol particles at velocities corresponding to their respective sizes. This results in collisions of the aerosol particles. Collisions produce coagulation in the case of solid particles and coalescence in the case of liquid particles. The resulting larger particles may then be collected by small-diam. multiple cyclones. An installation of a sonic precipitator unit built by Ultrasonic Corp., Cambridge, Mass., is shown (photo. and schematic drawing) attached to a contact H_2SO_4 plant.

64. Adadurov, I. E., & Gernet, D. V. The absorption of sulfuric anhydride by water vapor. Zh. Khim. Prom. 8, (18) 12-16 (1931); C.A. 26, 2279 (a) (1932).

From 6 to 8% of the SO_3 formed in the contact process is lost as an undissolved fog. If this fog is passed through water and then into a Cottrell app., the loss is reduced to 2.3-2.7%. However, the method is costly and complex. Between 338-450° SO_3 reacts with water vapor to form H_2SO_4 directly. If the fog is allowed to remain in contact with steam for 3-6 sec., reaction takes place, and 99% of the SO_3 is recovered in the condensed H_2SO_4.

65. Kraus, R. Method and apparatus for the analytical determination of sulfuric acid fogs applied to the roasting and contact gases of the sulfuric acid industry. Angew-Chem. 48, 227-8 (1935); C.A. 29, 4903 (3) (1935).

The gas contg. 0.35 vol. % SO_3 and other gases including SO_2 was saturated with water vapor at 100° and passed through a condenser at a velocity sufficiently slow to condense most of the water vapor. The product gas contained 0.06 vol. % SO_3 but retained all of the SO_2.

66. Remy, H., & Finnern, H. Fogs resulting from chemical reactions. IV. Adsorption of a chemical fog by a liquid and by solid materials. Z. anorg. allgem. Chem. 159, 241-255 (1926); C.A. 21, 1388 (1955).

The H_2SO_4 fog in a gas stream is effectively removed by injecting steam into the gas and then condensing the steam, whereby 98% of the H_2SO_4 in the gas stream is removed from the gas stream.

67. Remy, H., & Ruhland. The fogs occurring in chemical reactions. II. The absorption of chemical fogs. Z. anorg. allg. Chem. 139, 51-68 (1924); C.A. 19, 595 (7) (1925).

The rate of absorption of dry SO_3 and NH_4Cl fogs by aq. H_2SO_4 and NH_4Cl solns., resp., was found to depend on the concn. of the absorbing soln. The absorption rate-concn. curves are parallel to the corresponding b. p.-compn. curves. The rate of absorption of moist SO_3 or NH_4Cl decreases with increasing concn. of the absorbent.

68. Anon.-1965. A "fog broom" utilizing nylon thread. Chem. Week 97, Dec. 4, 1965. p. 79.

Laboratory experiments showed that a "tunnel visibility" could be made through heavy atmospheric fog in about 6 min. by a network of fine nylon threads wrapped around a revolving frame mounted on a truck travelling through the fog.

69. Anon.-1959. Fiber filters for fine acid mist. Brit. Chem. Eng. 4, 137 (Mar. 1959).

The filter is made of Terylene fiber or silicone (I.C.I. Silicone M441) coated glass fiber compressed to 2" thick pads either circular and made into tubes. (Forming temp. Terylene 140°-160°' Silicone-glass 400°-550°). H_2SO_3 mist $>$2 microns is completely removed (e.g. inlet gas contg. 0.1 g. H_2SO_4 gave a outlet gas contg. 0.0005-0.000 7 g. H_2SO_4 per cubic meter. Due to the hydrophobic nature of Terylene fiber, the mist collects on the filter in drops and falls off so that the filter is selfdraining. The fiber is 5-50 micron in diam. The unit is manufd. by Mancuna Eng. Ltd. and by Nordac Ltd. of England.

70. Brink, J.A., Jr. (Monsanto Chem. Co.) Monsanto solves air pollution problems with new fiber mist eliminator. Chem. Eng. 66, Nov. 16, 1959, p. 183-186.

A cartridge-type mist eliminator comprising a vertical sleeve of double-layer wire screen filled with a synthetic fiber packing has been developed for H_2SO_4 and H_3PO_4 mists and showed an efficiency of 99.95% on 0.3 to 3.0 micron particles under high gas velocity and low pressure drops, e.g. 400-500 ft/min. at 6-8 inches of water. Several full-scale installations (up to 20,000 SCFM) have been put into service to replace the electrostatic precipitators which were incurring excessive operating and maintenance costs. The capital cost of these mist eliminators (on the order of $50,000 for a 20,000 SCFM installation) is only a fraction of that for the electrostatic precipitator of the same capacity.

71. Brink, J.A., Jr., Burggrabe, W.F., & Rouscher, J.A. (Monsanto Co., St. Louis, Mo.) Fiber mist eliminators for higher velocities. Chem. Eng. Prog. 60, Nov. 1964, p. 68-73, cf. Chem. Eng. 66, Nov. 1959, p. 183-6; Phos. & Potas. (London) N 22, 28-29 (Apr.-May 1966).

A "high velocity" type of mist eliminator has been developed and improved. The performance characteristics of this mist eliminator as installed on top of H_3PO_4 and 99% H_2SO_4 absorption towers are given in 3 tables and 3 graphs. Examples: For H_3PO_4, gas velocity 600 ft/min., mist loading 28.2 mg. P_2O_5/SCF, removal efficiency 94.6%, pressure drop 9 inches water. For 99% H_2SO_4, gas volocity 600 ft./min., mist loading 18.6 mg. H_2SO_4/SCF., removal efficiency 97.3%, pressure drop 8 inches water.

72. Brink, J.A., Jr., Burggrabe, W.F., & Greenwell, L.E. (Monsanto Co., St. Louis, Mo.) Mist eliminators for sulfuric acid plants. Chem. Eng. Prog. 64, Nov. 1968, p. 82-86; cf. ibid., 60 Nov. 1964, p. 68-73; Chem. Eng. 66, Nov. 16, 1959, p. 183-6.

Knitted wire mesh made from 316 stainless steel (wire diam. 0.011 inch) has been extensively used to eliminate H_2SO_4 mists in the tail gas of contact H_2SO_4 plants, but stainless steel is subjected to excessive corrosion by 98-99% H_2SO_4 at 180-200°F. The latest innovation in H_2SO_4 mist elimination is to use Teflon fiber mats supported by special alloy grids. This type of demister collects H_2SO_4 mists of particle size less than 3 microns and for that purpose it is as efficient as the electrostatic precipitator. It costs more than the stainless steel wire mesh mist eliminator but much less than the electrostatic precipitator both in capital cost and in operating cost. Three types of H_2SO_4 mist eliminators are discussed: (1) The "spray catcher" comprising generally a 2-stage horizontal mat of knitted stainless steel wire mesh, glass fibers or synthetic fibers, supported by metal grids. (2) The "high velocity" mist eliminator comprising a Teflon fiber mat supported between alloy grids vertically disposed above the absorption tower, generally operated at gas velocities of 400-500 ft./min. (3) The "high efficiency" mist eliminater similar in principle as the high-velocity mist eliminator but operated at a much lower gas velocity, i.e., 15-40 ft./min. It is generally built in a multiple-cartridge form. The individual cartridges are constructed with two concentric alloy wire screens with fine Teflon fibers packed in the annular space between the two screens. The gas flows from the outside through the fiber packing and the collected H_2SO_4 drains down the inside surface of the cartridge to its closed bottom and is returned to the absorber through a liquid seal. The "high efficiency" mist eliminator works satisfactorily on 99% H_2SO_4 absorbers and on oleum towers. It is claimed that the removal efficiency on less than 3 micron H_2SO_4 mists is as high as 99.98%. Some operating characteristics of the three types of mist eliminators are given as follows:

(See next page for Table)

cont'd 72.

Table 1. Operating characteristics of various types of fiber mist eliminators as used on sulfuric acid plants.

	High Efficiency	High Velocity	Spray Catcher
Controlling mechanism for mist collection	Brownian Movement	Impaction	Impaction
Superficial velocity (ft./min.)	15 to 40	400 to 500	400 to 500
Efficiency on particles greater than 3 microns	Essentially 100%	Essentially 100%	Essentially 100%
Efficiency on particles 3 microns and smaller	95 to 99+%	90 to 98%	15 to 30%
Pressure drop ("W.C.)	5 to 15	6 to 8	½ to 1

73. Meinhold, T.F. (ed.) Three-way payout for H_2SO_4-gas cleaner. Chem. Processing 29, Mar. 1966, p. 63-64; cf. York, O.H., & Poppelle, E.W., Chem. Eng. Prog. 59, June 1963, p. 45-50.

The H_2SO_4 mist removal system at Chemicals, Inc., Bartow, Fla. was developed by York Separators, Inc. It is made of Teflon fiber materials supported by stainless steel grid. The mist remover was installed over the 20 ft. diam. SO_3 absorbers (2 used for the 900 tons/day plant). 56-87% of the H_2SO_4 mist particles measure less than 3 microns. The cleaned gas leaving a 206 ft. high stack contains about 0.6 mg. SO_3/SCF, which is well within the limit set by the State of Florida. The acid thus recovered amounts to 2.5 tons/day.

74. Morash, N., Krouse, M., & Vosseller, W.P. (National Lead Co., South Amboy, N.J.) Removing solid and mist particles from exhaust gases. Chem. Eng. Prog. 63, Mar. 1967, p. 70-74; C.A. 66, 118554 Z (1967).

An irrigated, thin, felted, fiber filter is described with a pilot-plant technique for the removal of submicron-size TiO_2 dust and H_2SO_4 acid mist particles from laden exhaust gases. Feeds contg. 0.44 g. TiO_2/ft.^{3} and 1.56 g. acid mist/ft.^{3} are exhausted with zero TiO_2 and 0.02-0.09 g. acid mist/ft.^{3}. Pressure drops of 5.5 to 10 in. water at gas flow rates of 1 to 5 ft./sec. are experienced. A min. flow rate of 8 gal. spray liquor/1000 ft.^{3} gas is required for high mist removal efficiencies. Both polyester and polypropylene fibers are evaluated.

75. York, O.H., & Poppele, E.W. (Otto H. York Co. Inc.) New acid gas cleaner for sulfuric acid plant. Paper presented at Air Pollution Control Association meeting, Jacksonville, Fla., Nov. 3, 1965; abst. Sulphur (London) No. 61, 30, (Dec. 1965).

In the new acid gas cleaner, a matrix of Teflon FEP fluorocarbon fibre is used to remove minute particles of sulphuric acid and oleum that appear in absorber effluent. Teflon was selected as the base material, partly for cont'd 75. its corrosion resistance and operating temperature range; and partly because it is strongly hydrophobic and produces good droplet formation. E.I. DuPont de Nemours and Co. Inc., which supplies the Teflon monofilament for the matrix, completed an investigative study which shows that the cleaner removes up to 98% of the particles even when acid entrainment is as low as 10 mg./cu. ft. The pressure drop in this instance was 6.3 in water. Comparing operating conditions in oleum plants, DuPont records that usually 92% to 94% of the entrained acid is removed only. Not only does the cleaner remove 98% of particles but in 98% sulphuric acid plants, 97% to 98% recovery of entrained acid is achieved. The new acid gas cleaner can be installed for between \$25,000 and \$50,000, and maintenance costs should be negligible. This compares with electrostatic precipitators, Venturi scrubbers, coke boxes and low velocity fillers which for a 500 to 1,000 tpd plant cost between \$100,000 and \$600,000, with operating costs as high as \$100,000 per year.

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76. Anthony, Jr., A.W. Two methods of wet scrubbing of gases for reduction of atmospheric pollution. Proc. Smoke Prevention Assoc. Am. 1948, 26 pp.; C.A. 43, 4405 e (1949).

The Venturi scrubber has been successfully applied to the removal of H_2SO_4 mist from gases using a high velocity for the gas stream through the Venturi tube and a moderate velocity for the water entering from outside into the throat of the Venturi. This arrangement replaces the more expensive electrostatic precipitator.

77. Chien, H.L. (Singyeh Sulfuric Acid Works, Shanghai, China). Venturi scrubbers. Chem. World (Shanghai) 14, 287-9 (June 1959) (Chemico translation TR-224).

The efficiency of a Venturi scrubber with water injected at the throat was investigated using, in one case, fluidized-bed pyrite roaster gas, and in another case, the tail gas of a H_2SO_4 contact process. In each case, the results were gratifying. The Venturi scrubbers were installed in the H_2SO_4 plant to replace the two electrostatic precipitators originally used. The Venturi scrubbers installed in the tail gas line have been in service over 3 years showing satisfactory performance. Typical operating data given as follows:

Table 1. Operating data of three-stage Venturi scrubbers using water injection at the throat.

	Gas Velocity m./Sec.	Pressure drop mm.H_2O	Dust or mist in feed gas g./cu.m.	Dust or mist in effluent g./cu.m.	Removal efficiency %
Dust removal	48	n.g.	13.1	0.103	99.4
	63	n.g.	6.84	0.0224	99.67
	80	300	n.g.	0.042	n.g.
Mist removal	100	450	5.00	0.015	99.7

n.g. Data not given in article.

78. Ekman, F.O., & Johnstone, H.F. (Univ. of Illinois, Urbana). Collection of aerosols in a Venturi scrubber. Ind. Eng. Chem. 43, 1358-1363 (1951).

For the removal of H_2SO_4 mist from gas streams using the Venturi scrubber, the following data are given:

Source of H_2SO_4 Mist	Gas Velocity at Throat-ft./sec.	Water Rate Gal./1,000 cu. ft. gas	Pressure Drop Inches Water	Mist Loading gal/cu. ft.		Removal Efficiency %
				In	Out	
Contact Acid Plant	171	4.3	9.7	190	0.6	99.7
Roaster Gas	171	7.2	14.5	309	1.7	99.4
Chloro sulfonic acid plant	---	---	---	756	7.8	98.9

79. Kristal, E., Dennis, R., & Silverman, L. (Harvard Univ. Cambridge, Mass.) Evaluation of an experimental French wet scrubber "Solivore". U.S. Atomic Energy Comm. Report NYO-4612, 1957, 50 pp.; C.A. 52, 7 f (1958).

An exptl. French wet scrubber, the Solivore, was tested for efficiency in removing air-suspended matter such as fly ash, coarse and fine H_2SO_4 mists, and Fe oxide fumes. This 600 cu. ft./min. unit has 4 collection stages in series, each contg. 2 1.5-horsepower, 9-gal./min., 7-lb./sq. in. spray generators, and a Venturi tube in which the gas attains a 12,000 cu.ft./min. max. velocity. The spray generators use a rotating mech. interrupter to disintegrate small liquid jets. Wt. collection efficiencies were detd. with inlet dust loadings of 0.2-2.0 grains/cu.ft. and water rates of 6-12 gal./min./spray generator for 1-2-, and 3-stage operation. Single-stage efficiencies were fly ash 99, coarse H_2SO_4 mist 95, Fe oxide fume 22, and fine H_2SO_4 mist 5%. Efficiency varied directly with the no. of collection stages and water rate, and inversely with the gas flow. Total pressure loss for one-stage operation (including droplet eliminator) was 4.5 in. of water at rated capacity. An addnl. pressure loss of 2-3 in. of water per stage was observed for multi-stage operation.

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80. Anon.-1967. Mahon's fog smog scrubber. Sulphur (London) No. 68, 35 (Jan.-Feb. 1967).

To clean particle-laden fumes from a 100 ton p.d. sulphuric acid concentrator, R.C. Mahon designed and built an air cleaner. The polluted air is sucked into three giant silo-shaped chambers and scrubbed with fog created jet-force streams of water broken up by 800 special nozzles. The resulting water-soaked whirlwind spins gases and contaminants at high angular velocity. The accumulated centrifugal force hurls the contaminants to the chamber's bottom, cont'd 80. where they are washed away. The fog-scrubbed air is discharged into the open. The unit is operated by Atlas Chemical Industries for the Volunteer Army Ammunition plant near Chattanooga, Tenn.

81. Richter, F. (Virginia-Carolina Chem. Corp., Richmond, Va.) Pollution control equipment pays off in two years. Air Eng. 2, 27-29, 53 (1960); C.A. 54, 20030 a (1960).

Air pollution by H_2SiF_6, SO_2, or SO_3 mists, and flakes of solid fluorides from the acidulation of phosphate rock dust with H_2SO_4 was controlled by low-velocity (490 ft./min.) cell-type, water scrubbers. The effluent passed through a series of five 24-ft. towers with water sprays discharging counter to the air flow.

82. Wong, J.B., Ranz, W.E., & Johnstone, H.F. (Univ. of Ill.) Inertial impaction of aerosol particles on cylinders. J. Appl. Phys. 26, 244-9 (1955); C.A. 49, 5038 f (1955).

The impaction of H_2SO_4 aerosols of nearly uniform size ranging from 0.6 to 1.4 micron in diam. on 2 Pt. wires, 29 and 83 microns in diam., and 2 W wires, 53 and 106 microns in diam. was measured at several velocities of flow past the wires. Reynolds numbers ranging from 13 to 330 were used. For values of the square root of the inertial parameter ψ below 1.4, the exptl. efficiencies of impaction agree with those predicted by Langmuir and Blodgett for potention flow and by Anandahl and Herrmann for a Reynolds number of 10. The exptl. values are higher than the calcd. values for $\psi^{1/2}$ greater than 1.4. The theoretical predication that a critical value of $\psi^{1/2}$ exists at approx. 1/4, below which inertial impaction does not occur was verified.

83. York, O.H., & Poppele, E.W. (Otto H. York Co. Inc.) Wire mesh mist eliminators. Chem. Eng. Prog. 59, June 1963, p. 45-50.

The operating characteristics of knitted wire-mesh and synthetic fiber mat mist eliminators are discussed. Examples of practical applications are given among which are the demisters used in contact H_2SO_4 plants. Certain design data are also given. When synthetic fibers are used instead of knitted stainless steel wire mesh, the fiber mats are supported on stainless steel, Monel, Carpenter 20, titanium, or Hastelloy grids. A typical mist eliminator is composed of a Teflon fiber mat sandwiched between Hastelloy C grids.

84. Lamm, C., Schumann, H., & Klauss, J. Removal of nitrogen-oxide-containing sulfuric acid fumes. East Ger. Pat. 50 584 (Cl. C 01b) Oct. 5, 1966 (appl. Apr. 17, 1965); C.A. 66, 96985 m (1967).

Off-gases from a H_2SO_4 plant, contg. NO and SO_3 0.925 g./standard m.^{3} are passed at a velocity of 3.5 m./sec. through a 80-mm. high foam layer of 98% H_2SO_4. The resulting off-gases contain SO_3 0.04 g./m.^{3} and are free of NO.

85. Rosenbloom, W.J. (Chem. Construction Corp.) Recovery of oxides of sulfur and fluorides from gas mixtures. U.S. Pat 3 031 262 Apr. 24, 1962 (appl. Feb. 27, 1959); C.A. 57, 10781 e (1962).

Off-gases from the calcining of phosphate rock are (1) scrubbed with H_2SO_4 in a spray chamber to cool the gases and to remove SO_3 and particulate material, (2) scrubbed with NH_4 sulfite-bisulfite soln. in an absorption tower to remove SO_2 and HF, (3) discharged to the atm. The liquid stream from the absorption tower is (1) autoclaved with air to oxidize $(NH_4)_2SO_3$; (2) treated with a metal sulfate (e.g. $MgSO_4$) to ppt. metal fluoride; (3) filtered to remove solids, including SiO_2; and (4) crystd. to recover $(NH_4)_2SO_4$.

86. Tigges, A.V. (to Air Preheater Corp.) Recovering heat and sulfur compounds from hot gaseous products of combustion. U.S. Pat. 2 863 723 Dec. 9, 1958; C.A. 53, 5645 c (1959).

The gases may be cooled below their dew point if the heat-exchange surfaces, e.g. rotary regenerative air preheaters, and sprayed with noncorrosive 70% H_2SO_4. The acid is reclaimed with the recovery of absorbed SO_2 or SO_3.

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87. Chem. Construction (G.B.) Ltd. (Syers, R., inventor) Removal of sulfur oxides from flue gases and stack gases. Brit. Pat. 826 221, Dec. 21, 1959; C.A. 54, 10289 h (1960).

NH_3 is added to flue gas or H_2SO_4 plant stack gas at a temp. higher than the dew point of the flue gas or the stack gas. The SO_2 and SO_3 present in the flue gas or the stack gas are converted to solid $(NH_4)_2SO_3$, $(NH_4)_2SO_4$, and NH_4HSO_4 which is removed from the flue gas or the stack gas by passage through an electrostatic precipitator or a cyclone. The process reduces the air pollution caused by the flue gas or the stack gas.

88. Momose, S. (Chubu Elec. Power Co., Nagoya, Japan) The prevention of corrosion by sulfuric acid of heavy oil burners. Netsu Kanri 10, No. 10 20-22 (1958); C.A. 53, 19349 a (1959).

cont'd 88. The stack gas of an elec. generating boiler system which burns heavy oil contg. 2.8-3.0% S is reacted with NH_3 gas to reduce the amt. of SO_3. The dew point dropped sharply (from 140 to 45^{o}) by blowing 0.01-0.02% NH_3 with respect to the oil. The dew point of the flue gases with addn. of 0.02-0.12% NH_3 (based on wt. of oil) was almost const. at 45^{o}.

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89. Hohmann, H. Removal of sulfur dioxide and SO_3 from exhaust gases. East Ger. Pat. 55 743 (cl. B 01d) May 5, 1967 (appl. Aug. 25, 1966); C.A. 67, 76124 x (1967).

The process is to pass the exhaust gas through a mill contg. $CaCO_3$ before being sent to the chimney. The $CaCO_3$ is granulated and dried in the mill and as a result the mill contains 50-100%, relative water vapor, and the adsorbent has a large surface area. SO_2 is removed from the gas by adsorption on $CaCO_3$ and the formation of $CaSO_3 . 1/2H_2O$.

90. Lowenstein-Lom, W.G. (to Standard Oil Dev. Co.) Removal of sulfur oxides from flue gases and their conversion to ammonium sulfate. Brit. Pat. 708 095, Apr. 28, 1954; C.A. 48, 11033 c (1954).

Gases contg. $S0_2$ and $S0_3$ are scrubbed with an aq. suspension of $Mg(0H)_2$. The spent scrubbing soln. now contg. $MgSO_3$ and $MgS0_4$ is aerated and oxidize $MgS0_3$ into $MgS0_4$. After this operation the solution is treated with NH_3 gas to convert $MgS0_4$ into $Mg(0H)_2$ and $(NH_4)_2S0_4$. The $Mg(OH)_2$ separated and used to make a fresh suspension for scrubbing. The $(NH_4)_2S0_4$ soln. is concentrated to crystallize the $(NH_4)_2S0_4$.

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91. Dr. C. Otto & Co. GmbH. (Struck, C.H., inventor.) Removal of sulfur oxides from industrial gases. Ger. Pat. 1 234 912 (cl. F 23j) Feb. 23, 1967 (appl. Dec. 2, 1961); C.A. 66, 97014 f (1967).

SO_2 and SO_3 are removed from gases by washing with a 35-80% H_2SO_4 soln. contg. peroxysulfuric acid (I) equiv. to 5-60 g. H_2O_2/l. at a temp. $>60^{o}$ which is also in excess of the dew point of the gas being cleaned. The H_2SO_4 formed is continuously removed and the used I is regenerated by anodic oxidn. The gas may be subjected to previous mech. cleaning and (or) be cooled to room temp. and reheated for cleaning. Thus, to clean at 80^{o} a gas having a dew point of 70^{o}, a 5-15 sec. contact with 37% aq. H_2SO_4 contg. the equiv. free O_2 of 20 g. H_2O_2/l. is satisfactory.

92. Simon-Carves Ltd. Sulfur oxides elimination in residual gases. Belg. Pat. 613 590, Feb. 28, 1962 (Brit. appl. Feb. 25, 1961); C.A. 57, 9460 c (1962).

SO_2 and SO_3 were extd. from fumes and chimney gases by passing the ascending gases through a 40-80% aq. H_2SO_4 spray contg. peroxydisulfuric acid (I) and H_2O_2. Part of the wash soln. was recycled, part withdrawn and and treated for H_2SO_4 recuperation and an equiv. amt. of H_2O added, and part cooled and regenerated by an electrolytic cell to strengthen I and H_2O_2, this being facilitated by halide ion addn. To recuperate HCl-free H_2SO_4, either the gases were first H_2O washed, or the recuperated H_2SO_4 distd.

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93. Crossley, H.E. (Fuel Research Station, D.S.I.R., Greenwich, England.) The reduction of sulfur trioxide by constituents of boiler-flue dust. J. Inst. Fuel 21, 207-9, 213 (1948); C.A. 42, 4326 g (1948).

Boiler plants fired by pulverized fuel are relatively immune from the corrosion and deposit difficulties sometimes encountered on the external heating surfaces when mech. stokers are used. An investigation of the reduction of SO_3 to SO_2 indicates that this immunity may be partly due to the presence of fly-ash particles rich in magnetite, Fe_3O_4. Magnetite reduces SO_3, the action being most pronounced at temps. above 500°. Coke, also present in flue dust, reduces SO_3 at temps. below the ignition point of the coke. The remaining fraction of the flue dust from powd.-fuel-fired boilers had little, if any, reducing action on SO_3. It seems possible the the max. possible reduction of SO_3 in a boiler might be secured by introducing the coarser part of the magnetic fraction of powd.-coal fly-ash into the gas in the combustion chamber, with a view to the deposition of some Fe_30_4 on the heating surfaces where the reduction takes place. The best method of reducing the SO_3 by C would probably be the introduction of a C smoke near the boiler outlet, or the arrangement of a bed of suitably sized carbon or coke across the gas stream in the duct between the boiler and the economizer. In this position the temp. of the flue gas is usually 300°, and there should be little loss of C by burning. In the lab. expts. the efficiency of reduction of SO_3 by coke was 100% at 350°.

94. Hansen, W. The reduction of sulfur trioxide by solid particles in flue gases. Oelfeuerung (Stuttgard, Germany) 6, 90-94 (1961); C.A. 56, 7619 b (1962).

SO_3 in a stream of N is reduced to SO_2 when passed through a reaction tube contg. black fly ash or Fe_3O_4 at 300-700° or fly coke at 200-700°. White fly ash and SiO_2 are less effective. SO_3 in a stream of N, O, and H_2O is reduced to SO_2 when passed over fly coke, gas coke, or smelting coke at 350° or Fe_3O_4 at 500-650°. Essentially no SO_3 remained in the reaction tubes contg. coke or SiO_2. A layer of Fe_2O_3 retained 97% of the entering SO_3 as SO_4^{--} at 350-500°. Fe_3O_4 retained 37 and 34% resp., at these temps.

95. Siemes-Schuckertwerke AG. Separating a constituent from a gas stream. Brit. Pat. 1 003 419 (Cl. B 04 b, c) Sept. 2, 1965, (appl. June 21, 1963); C.A. 63, 14405 g (1965).

Finely divided (<6 micron) Fe_2O_3 is sprayed into a flue-gas stream at 250° to remove SO_2 and SO_3: $2Fe_2O_3 + 6SO_2 + 3O_2 \rightarrow 2Fe_2(SO_4)_3$ and $Fe_2O_3 + 3SO_3 \rightarrow Fe_2(SO_4)_3$. The sped. $Fe_2(SO_4)_3$ is decompd. at 500° to recover Fe_2O_3 and SO_3 for conversion to H_2SO_4.

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96. Feustel, K., Johswich, F., & Stratmann, H. (to Reinluft GmbH, Germany). Removal of sulfur oxides from fuel gases. U.S. Pat. 2 992 065 July 11, 1961; C.A. 55, 26390 b (1961).

A hot gas stream contg. SO_2 and SO_3 is passed over a carbonaceous absorbent, e.g. charcoal, at 150-250° to absorb SO_3. The gas is then cooled to 100-50° and passed over the absorbent to remove SO_2. The absorbent is then heated to reduce SO_3 to SO_2, and then the SO_2 is purged from it.

97. Oesterreichische Stickstoffwerke AG. (Huber, F., inventor.) Portland cement. Austrian Pat. 195,830, Feb. 25, 1958; C.A. 52, 6756 g (1958).

In a process of the manuf. of portland cement from cement raw material, e.g. clay and lime contg. small amts. of sulfatic impurities, the powd. raw material is mixed with small amts. of solid fuels, approx. sufficient to reduce its SO_3 contents, and the mixt. is calcined in an inert gas atm. before formation of the clinker. Preferably N or the gas from the end zone of the calcination furnace is used as inert gas, and the reduction treatment is conducted in the same furnace as the formation of the clinker.

98. Vitukhnovskaya, M.S., & Belyanskaya, E.A. The use of reducing agents for the regeneration of the spent sulfuric acid. Zh. Prikl. Khim. 33, 2427-2434 (1960); C.A. 55, 7769 d (1961).

The kinetics of reduction of SO_3 to SO_2 was studied by passing mixts. of SO_3 and N with and without CO through an empty reactor, retention 0.2 min., and through a reactor filled with activated C, retention 0.09 min. The amt. of SO_2 formed, x, at 800° under all conditions increased as the concn. of SO_3 in the initial gas increased from 1 to 17%. The presence of CO increased x very little. x increased with the temp. in the 500-800° range, but at all temps. it was much higher over activated C than with CO, despite the lower retention time. The difference increased at higher temps. Even at 500° x was higher over C (86%) than at 700° with CO. At 700° over C, x = 96%. Reducing with C at 800° resulted in the formation of S. The rate of reaction $2SO_3 + C \rightarrow 2SO_2 + CO_2$ passed through a max. at 500°; that of $SO_3 + C \rightarrow SO_2 + CO$ decreased as the temp. increased from 400 to 700°, and that of $2SO_3 \rightarrow 2SO_2 + O_2$ increased at first slowly below 600° and very rapidly above 600°.

99. Wahnschaffe, E. Desulfurization of smoke gases by the clear-air method. Mitt. Ver. Grosskesselbesitzer No. 83, 72-74 (1963); C.A. 59, 3254 b (1963).

From 1000 to 2000 cu. m./hr. fuel oil combustion gas, emanating at a temp. of 200° is passed through a precooler, a cooler, a reusable semicoke absorber to remove SO_2 and SO_3, a desorber, and a heater (to 400°) for desorbed gases to remove the S-content in the form of pptd. S. The app. operated satisfactorily under a wide range of industrial conditions.

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100. Mandelik, B.G. (to Chem. Construction Corp., New York, N.Y.) Complete recovery of sulfur dioxide. U.S. Pat. 3 059 995 (Cl. 23-177), Oct. 23, 1962 (appl. May 11, 1960); C.A. 58, 2190 e (1963).

The off-gas derived from sulfating roast of sulfide ores at 400-800° contg. 0.5-3% SO_3, 6-9% SO_2, and entrained dust was heated to 900-1400° by burning H_2S, refinery sludge acid, natural gas within the gas stream with air addn. if required, thus decompg. the SO_3 to SO_2 and O and recovering all S values; SO_3 remaining is $< 0.05\%$. The hot gas stream partially cooled by a waste heat boiler to approx. 350° was then H_2O-scrubbed, further cooling it and eliminating the dust.

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101. Cerny, F. Recovering sulfur oxides from combustion products. Czech. Pat. 100 363, July 15, 1961 (appl. Aug. 5, 1958); C.A. 58, 2190 f (1963).

When the combustion gases are cooled below the dew point prior to escapting into the atm., the resulting condensate absorbs entire SO_3 and a part of SO_2, another part of which is bound by the wet volatile ashes. Addn. of steam to the combustion gases aids the effect by cooling the gases and increasing the dew point of the products.

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102. Hrdlicka, K. Absorbing sulfur dioxide and trioxide from industrial fumes by the zinc method. Czech. Pat. 90 701, June 15, 1959; cf. Tech. Chem. (Prague) 12 (5), 236-241 (1962); C.A. 54, 9230 d (1960); 61, 3608 c (1964).

The SO_2- and SO_3-containing gas is scrubbed with an aqueous slurry of $Zn(OH)_2$. The liq. effluent from the scrubber contains $Zn(H_2SO_3)_2$, $ZnSO_4$ and crystaline $ZnSO_3$-2.5H_2O. This effluent is treated in either of the following two ways: (1) thermal decomposition of $Zn(HSO_3)_2$ and $ZnSO_3 \cdot 2.5 H_2O$ to give SO_2 gas and regenerate ZnO; (2) adding H_2SO_4 to drive off SO_2 and recover $ZnSO_4$ as a byproduct.

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103. Anon. -1969. Controlling the SO_3 content of industrial flue gases. Sulphur (London) No. 82, 30-31 (May-June 1969).

The Siemens "Sulfotherm" continuous analyzer is briefly described. It takes a gas sample at 450°C, filters it and mixes it with water vapor at 200°C. The SO_3 in the sample reacts with water vapor to from H_2SO_4 which is condensed. The condensed H_2SO_4 is reheated to 100°C to drive out any SO_2 and CO_2. The H_2SO_4-contg. liquid is again cooled and its electric conductivity is measured and recorded in terms of SO_3 content in the gas. Four scales are provided on the instrument, the lowest covers the SO_3 range 0-100 mg. /cu. m., and the highest scale 600-3500 mg. /cu. m.

104. Central Electricity Generating Board (Jackson, P. J., & Laxton, J. W., inventors.) Measurement of gas concentration in gas mixtures. Brit. Pat. 1 030 541 (Cl. G 08c) May 25, 1966 (appl. Jan. 2, 1964); C. A. 65, 3006 a (1966).

The gas mixt. is passed at a known rate into an extractor to dissolve a particular gas. The subject soln. is passed through a reactor bed which contains a reagent capable of giving a colorimetric response to the particular gas. An optical cell is filled with the colored soln. for photo-elec. detn. of the absorbance. Thus, SO_3 is removed from flue gas by aq. (preferably 4:1 vol. /vol.) iso-PrOH prior to reaction with Ba chloroanilate which liberates reddish acid chloroanilate ions with max. absorption at 535 m micron. The method is good to 0.2 ppm. and is particularly suitable for flue gases from oil-fired boilers.

105. Corbett, P. F. (Brit. Coal Utilization Research Assoc.) The determination of sulfur dioxide and sulfur trioxide in flue gases. J. Inst. Fuel 24, 247-251 (1951); C. A. 46, 237 i (1952).

A method is described for the determination of small traces of SO_3 in the presence of a large excess of SO_2 by using 80% iso-propanol both as the oxidation inhibitor and absorbent.

PART IV

Chemical Construction Corporation
CONSULTING DIVISION

A BIBLIOGRAPHY OF REMOVAL OF NITROGEN OXIDES FROM WASTE GASES, EXCEPT METHODS BASED ON REDUCTION AT HIGH TEMPERATURE AND CATALYTIC DECOMPOSITION

1907-1968

WITH ABSTRACTS

TABLE OF CONTENTS
(Subject Index)

PART ONE

Removal of Nitrogen Oxides From Chamber-and Mills-Packard Sulfuric Acid Plant Tail Gases

		Ref. No.
I	Absorption in concentrated sulfuric acid	1 to 8
II	Absorption in ammoniacal solutions	9, 10, 39
III	Reaction with ammonia in the vapor phase	11, 12, 13
IV	Absorption in sodium hydroxide solutions	14
V	Addition of fine water spray before electrostatic precipitation	15
VI	Adsorption on active carbon	16, 17
VII	Adsorption on phosphates	18
VIII	Adsorption on fluidized peat	19

PART TWO

Removal of Low Concentrations of Nitrogen Oxides From Waste Gases

			Ref. No.
I	Nitrogen oxides (NO + NO_2) removal by absorption		
	a.	Absorption in water	20 to 29, 149
	b.	Absorption in sulfuric acid and H_2SO_4-HNO_3 mixtures	30 to 37
	c.	Absorption in ammoniacal solutions	38 to 44
	d.	Absorption by ammonia in the vapor phase	45 to 49
	e.	Absorption in alkaline solutions	27, 50 to 56, 61, 121
	f.	Absorption in carbonate solutions	57 to 74
	g.	Oxidation - scrubbing	75 to 82
	h.	Absorption in ferrous salt solutions	83 to 89
	i.	Absorption in sulfite solutions	90 to 92
	j.	Absorption in calcium and/or magnesium oxide and hydroxide slurries	93 to 101
	k.	Absorption in limestone slurries or with wet limestone	102, 103
	l.	Absorption by moist iron on manganese oxides	104 to 106
	m.	Absorption by iron sulfide	107 to 109
	n.	Absorption by dry oxides and hydroxides	110 to 115, 140
	o.	Absorption in aqueous organic solutions	116 to 121
	p.	Absorption in anhydrous organic liquids	122
II	Nitric oxide, NO, removal by adsorption		
	a.	Adsorption on active carbon	123 to 125
	b.	Adsorption on alumina	126
	c.	Adsorption on clay	127
	d.	Adsorption on graphite	128
	e.	Adsorption on silica gel	129 to 132
	f.	Adsorption on zeolite	133, 134
III	Nitrogen oxides (NO + NO_2) removal by adsorption		
	a.	Adsorption on active carbon	135 to 140
	b.	Adsorption on aluminum silicate	141 to 143
	c.	Adsorption on silica gel	26, 144 to 151, 153, 154

		Ref. No.
d.	Adsorption on zeolite	150, 152 to 155
e.	Adsorption on ion-exchange resins	156, 157
f.	Adsorption on peat	158

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PART ONE

Removal of Nitrogen Oxides From Chamber-and Mills-Packard Sulfuric Acid Plant Tail Gases

1. Beavers, G.E. Absorption of nitrogen oxides in the chamber acid process. Chem. Met. Eng. 32, 280-2 (1925); C.A. 19, 1328 (1) (1925).

   At Copper Hill, Tenn., the tail gases from the chamber H_2SO_4 plant was scrubbed with H_2SO_4 as the absorbent. The efficiency of N oxides absorption was investigated with respect to the sp.g., purity and temperature of H_2SO_4. It was found that the amount of N oxides absorbed increases directly with the sp.g. and the purity, and inversely with the temperature.

2. Bylov, V.D., Znamenskii, Yu. D., Kapitonova, L.P., & Shchedrov, M.S. Scrubbing nitrogen oxides from partially oxidized gases with sulfuric acid. Zh. Prikl. Khim. 35, 1503-5 (1962); C.A. 57, 12098 i (1962).

   The efficiency of absorption of nitrogen oxides in 93% H_2SO_4 is materially increased if the nitorgen oxides are first oxidized, for example, by passing them through a 93% H_2SO_4 containing 3-4% HNO_3. This increase was shown to be from 41.5% to 79%. In a laboratory set-up, a column 2 m. high having 8 bubble plates was used. The lower 2 plates were irrigated with the HNO_3-H_2SO_4 mixture and the upper 6 plates by 93% H_2SO_4.

3. Fairlie, A.M. Recovering nitrogen oxides in sulfuric acid manufacture. U.S. Pat 1 420 477, June 20, 1922; C.A. 16, 2969 (2) (1922).

   SO_2 is removed from exit gas of a H_2SO_4 plant by oxidation, and lower N oxides are then oxidized to higher oxides and absorbed.

4. Kuz'minuikh, I.N. Calculation of Gay-Lussac towers and their rationalization. Khimstroi (U.S.S.R.) 7, 278-285 (1935); C.A. 29, 7023 (6) (1935).

   A discussion of the physicochem. processes of the absorption of N oxides and math. treatment of the efficiency of the Gay-Lussac towers are given. The vol. of the towers can be decreased by sepg. the processes of absorption and oxidation, by increasing lineal velocity of gas currents and by substituting Raschig rings for quartz packing.

5. Kuz'minuikh, I.N. & Yudina, V. The influence of gas volocity on the absorption velocity of nitrogen oxides by sulfuric acid. Khimstroi (U.S.S.R.) 6, 315-317 (1934); C.A. 29, 7023 (6) (1935).

   Lab. expts. showed that the velocity of N_2O_3 absorption by H_2SO_4 is influenced not only by the acid concn. and temp. but also by the lineal velocity of gas currents in the Gay-Lussac tower.

6. Lamm, C., Schmann, H., & Klauss, J. Removal of nitrogen-oxide-containing sulfuric acid fumes. Ger. (East) Pat. 50 584 (Cl. C 01b) Oct. 5, 1966 (appl. Apr. 17, 1965); C.A. 66, 96985 m (1967).

   Off-gases from a H_2SO_4 plant, contg. NO and SO_3 0.925 g./standard m.^{3} are passed at a velocity of 3.5 m./sec. through a 80-mm high foam layer of 98% H_2SO_4. The resulting off-gases contain SO_3 0.04 g./m.^{3} and are free of NO.

7. Malin, K.M. Ways of decreasing the volume of Gay-Lussac towers. Khimstroi (U.S.S.R.) 7, 269-277 (1935); C.A. 29, 7023 (7) (1935).

   Various measures proposed for the reduction of the vol. of the Gay-Lussac towers, were critically reviewed, and considered of no practical value unless adequate means for likewise reduction of the time required for the oxidation of NO is used. Of all the technological factors, that of the temp. regime is of greatest importance. A reduction of temp. results in the decrease of the vol. of Gay-Lussac tower and smaller consumption of HNO_3.

8. Safiullin, N. Sh., & Olevinskii, M.I. Rendering harmless the tail gases from sulfuric acid chamber process. Khim. Prom. 1955, 132-6; C.A. 50, 541 f (1956).

   A dependable purification method for the tail gases in the H_2SO_4 chamber process consists in passing the gas through a tower contg. a checker-work sprayed with concd. H_2SO_4 (88 + %) and through a wet electrostatic filter. The H_2SO_4-fog concn. in the effluent vapors is lowered to 0.04-0.10 g./cu. m. The N oxides are almost completely absorbed, and the specific-HNO_3 consumption is reduced by 6-8 kg./ton of H_2SO_4 produced, when compared with other purification methods.

9. Varlamov, M. L., Manakin, G. A., Zbrozhek, L. S., & Starosel'skii, Ya. I. Ammonia method for removing nitrogen oxides from exhaust gases of a sulfuric acid system. II. Nauchn. Zap. Odessk. Politekhn. Inst. 40 34-44 (1962); C.A. 59, 234 f (1963).

An exptl. industrial app. (capacity 250-500 cu. m. gas/hr.) consisting of 2 scrubbers and an elec. filter was tested. Operating without an oxidizing medium, the av. removal of acid components was 74.3%. In the 1st scrubber the acid component content was reduced by 2/3 by aq. NH_3 and in the elec. filter by only 5%; in the 2nd scrubber NH_3 was removed. With an oxidizing medium at a capacity of 280-500 cu. m./hr., 77.4% of the acid components were removed. The NH_3 concn. in the soln. for the 1st scrubber was 0.74-1.97%, the liquid rate was 11-20 cu. m./hr.-sq. m., and the pressure drop of the app. was 29-198 mm. H_2O. The gas is cooled by evapn. of H_2O from the solns. thus making it possible to use weak NH_3 solns. as well as $(NH_4)_2CO_3$.

10. Varlamov, M. L., Manakin, G. A., Zbrozhek, L. S., & Starosel'skii, Ya. I. Study of the ammonia method for the removal of nitrogen oxides from waste gases from the towers of the nitroso-sulfuric acid system. Zh. Prikl. Khim 36 (11), 2335-2343 (1963); C. A. 60, 6513 f (1964).

The scrubbing of N oxides from the stacks of the chamber acid process with aq. NH_4OH was studied in a pilot plant with packed columns. With a liquor rate of 11-20 cu. m./cu. m. hr. of 0.74-1.97% NH_4OH the degree of purification, α, from a gas contg. 0.379% acid gases was 74.3-77.4%. The exit gases contained 0.0764% ($NO + NO_2 + 2SO_2$). Increasing NH_4OH from 1 to 1.67% did not affect α. In a foam app. with a capacity of 20 cu. m./hr. gas, $\alpha = 90\%$, reducing the content of N oxides to 0.03% in the stack gases below the amt. of sanitary requirements.

11. Varlamov, M. L., Manakin, G. A., Starosel'skii, Ya. I., & Zbrozhek, L. S. Ammonia method for removing nitrogen oxides from exhaust gases of a tower nitrose sulfuric acid system. Nauchn. Zap. Odessk. Politekhn. Inst. 40, 24-33 (1962); C. A. 58, 13485 f (1963).

A study was made of an NH_3 method for removing low concns. of N oxides from exhaust gases, by using NH_3 and NH_4OH. By using NH_3 and acoustical coagulation of aerosols the av. degree of purification was 85% with a high degree of oxidn. of NO in gases subjected to treatment. The completeness of the reaction of NO_2 and an equimol. mixt. of $NO + NO_2$ with NH_3 was 82-93% and increased slightly with increase in the reaction space. A lab. study was made of refining of exhaust gases of a tower nitrose H_2SO_4 system by using a gas lift with NH_4OH and an elec. filter for removal of aerosols. The av. degree of refining was 63.6% with a degree of oxidn. of NO in the treated gases of 40%. If the NO in the exhaust gases was insufficiently oxidized, the degree of purification was less.

12. Varlamov, M. L., Manakin, G. A., Staroselskii, Ya. I., & Zbrozhek, L. S. Investigation of the ammonia method for the purification of gases from low concentrations of nitrogen oxides. Zh. Prikl. Khim. 36, 8105 (1963); C. A. 59, 239 b (1963).

Lab. scale investigations were carried out on the NH_3 method of purification of gases from low concns. of N oxides, by using gaseous NH_3. In using acoustic coagulation of the NH_4NO_2 and NH_4NO_3 aerosols, the degree of removal of the N oxides is ~85% and does not depend on excess NH_3 in the gas mixt. Completeness of the reaction of NO_2 and equimol. mixts. of NO and NO_2 with gaseous NH_3 averages 81-91.4% and increases little with increase in the reaction vol. The NH_3 method of gas purification was investigated in a H_2SO_4 tower system on lab. equipment by using gas-lifting app. and electrofilters for the removal of NH_3 compds. from the exhaust gases. The lower degree of purification of production-scale gases compared to that obtained under lab. conditions is primarily due to the lower degree of NO oxidn. in the inflowing gases. However, with a recalcn. of the compn. of the oxides to an equimol. mixt. of NO and NO_2, the degree of purification of production gases reasonably approaches that obtained in the lab. expts.

13. Varlamov, M. L., Manakin, G. A., Zabrozhek, L. S., & Starosel'skii, Ya. I. Purification of gases of tower nitrose sulfuric acid systems. Sb. Tr. Odessk Med. Inst. 1961, No. 15, 44-51; C. A. 57, 14703 i (1962).

The removal of N oxides from waste gases of H_2S production by the tower process by means of a reaction with NH_3 gas was studied; an aerosol of NH_4-nitrite-nitrate is thus formed. The size of the reaction space has little effect on this process; 93% reaction is achieved. The effect of the concn. of N oxides and NH_3, the degree of NO oxidn., and the time of sound treatment on the acoustical coagulation of the above aerosol were studied. The degree of purification reached 87%. Trapping of the aerosol (produced by the reaction of waste gases in NH_3 water in a gas-lift app.) in an elec. filter was studied. At 30.7 and 44% oxidn. of NO, the degree of purification was 51.2 and 80.4%, resp. The content of N oxides in the gases as a result of such purification can be increased by increasing the degree of NO oxidn. and by using optimum conditions. In an alk. medium at $<70^{\circ}$, decompn. of NH_4-NO_2 is negligible.

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14. Varlamov, M. L., Manakin, G. A., Zbrozhek, L. S., & Starosel'skii, Ya. I. Purification of exhaust gases of a nitrose-sulfuric acid system in a foam apparatus at a pilot plant installation by using water and caustic soda. Izv. Vyssh. Ucheb. Zaved. Khim. i Khim. Tekhnol. 10 (8), 948-9 (1967); C. A. 68, 14557 c (1968).

14. Cont'd Nitrous gases from a nitrose-H_2SO_4 system at rates up to 1500 $m.^3$/hr. were scrubbed, in pilot plant studies, to remove acid components and N oxides with H_2O and with 1.5-3% NaOH soln. in a 4-tray, 0.5-m. diam., perforated plate column. The av. degree of removal of acid components was 41.7%, and that of N oxides was 28%. These values correspond to absorption coeffs. of 0.204 and 0.124 1./sec., resp.

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15. Wolf, F., Stopperka, K., & Huhn, J. Procedure for removal of polysulfuric acid aerosol, nitrogen compounds, and nitrogen oxides from exhaust gases of sulfuric acid manufacture. Ger. (East) Pat. 30 164 (Cl. C 01b), Jan. 5, 1965 (appl. Sept. 23, 1963); C.A. 63, 9507 g (1965).

Addn. of 30 to 50 ml. of H_2O as fine mist to 1000 $m.^3$ of gases eliminates in one operation polysulfuric acid aerosol, SO_3, N_2O, NO_2, and all nitrosyl compounds. The nitrosyl compds. formed are electrostatically pptd.

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16. Feustel, K., Johswich, F. & Stratmann, H. (to Firma Reinluft GmbH, Germany). Process for recovering oxides of nitrogen and sulfur from gaseous mixtures. U.S. Pat 2 992 895, July 18, 1961 (appl. in Germany Aug. 28, 1957).

A process is specified in which a gas contg. N oxides and S compounds is heated above 300°C in contact with a carbonaceous material in the presence of O_2. Then the hot gas is cooled to below 300°C. and contacted with active carbon to adsorb the N and S oxides. The active carbon is subsequently regenerated by heating to above 300°C. The process is continuous using moving beds and a recycling system.

17. Universal Oil Products Co. (U.S.) Recovery of nitrogen oxides. Neth. Pat. Appl. 6 607 036 (Cl. B 01 d) Nov. 25, 1966 (U.S. appl. May 24, 1965); C.A. 66, 87195 b (1967).

Oxides of N can be recovered from tail gases of NHO_3 or H_2SO_4 plants by adsorption on activated carbon. After sorption, they can be stripped by steam or hot air and fed back to the process. The temp. of the stripping medium must be higher than the crit. temp. of N dioxide. For continuous operation, 2 beds are used, operating cyclically.

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18. Gauz, S.N., & Kuznetsov, I.E. Purification of the discharge gases from sulfuric acid tower systems. U.S.S.R. Pat. 181 061 (Cl. C 01b, B 01d) Apr. 15, 1966 (appl. May 17, 1965); C.A. 65, 8401 h (1966).

The discharge gases are purified by the sorption of the N oxides, the H_2SO_4 fog, and the H_2SO_4 spray by a phosphate raw material (apatite concentrate and phosphates) in a fluidized bed app. to increase the degree of purification.

19. Kuznetsov, I.E., Ganz, S.N., & Shlifer, V.A. Purification of gases of sulfuric acid Mills-Packard systems from nitrogen oxides and other contaminants by peat-alkaline sorbent. Izv. Vyssh. Ucheb. Zaved., Khim. i Khim. Tekhnol. (U.S.S.R.) 10 (7), 797-801 (1967); C.A. 67, 110130 h (1967).

Expts. were carried out in order to study the use of peat as an adsorbent for common contaminants of the chamber process H_2SO_4 plant exit gases (i.e. N oxides, SO_2, and mist and droplets of H_2SO_4). The gas stream passed through a fluidized bed of peat in a continuous reactor. The effect of depth of the bed, gas velocity moisture content of peat, and concn. of the resp. contaminants on the efficiency of adsorption was studied. Contact of higher N oxides with wet peat brings about formation of NHO_3 that oxidizes and nitrates the adsorbent yielding an org.-mineral fertilizer. NO is not adsorbed as such but is readily oxidized during its contact with the peat surface which apparently acts as an oxidn. catalyst. Addn. of CaO, Na_2CO_3 (2%), or NH_3 (1%) brings about marked increase in adsorption of SO_2 and H_2SO_4 mist and droplets. To treat 1000 m.^{3} of gas, 15-20 kg. of peat (50% H_2O) and 1.5-2.0 kg. of NH_3 are necessary. The depth of the fluidizing bed should be 0.8-1.0 m., the ratio fresh: recycled adsorbent = 1:2, and retention time of the adsorbent 5-6 hrs. The degree of adsorption of S compds. and N oxides is almost 100 and 90-2%, resp. The fertilizer produced contains up to 15% of N and 30% of available humic acids.

Chemical Construction Corporation
CONSULTING DIVISION

A BIBLIOGRAPHY OF REMOVAL OF NITROGEN OXIDES FROM WASTE GASES, EXCEPT METHODS BASED ON REDUCTION AT HIGH TEMPERATURE AND CATALYTIC DECOMPOSITION

1907-1968

WITH ABSTRACTS

PART TWO

Removal of Low Concentrations of Nitrogen Oxides From Waste Gases

20. Andersen, L.B., & Johnstone, H.F. (Univ. of Ill.) Gas absorption and oxidation in dispersed media. J. Am. Inst. Chem. Engrs. 1, 135-141 (June, 1955).

The absorption and subsequent liquid-phase reaction of oxygen was studied with two types of dispersion apparatus, the Venturi atomizer and the fritter-glass disperser. The systems studied in both devices included the absorption of atmospheric oxygen by catalyzed sodium sulfite solutions and the simultaneous absorption of atmospheric oxygen with nitrogen dioxide and with sulfur dioxide by water. Very large values of the liquid-film mass transfer coefficient for oxygen absorption were observed in the atomization zone of the Ventrui atomizer. Over-all recovery efficiencies were less than 2.3% for nitrogen dioxide but reached as much as 22% for sulfur dioxide. Oxidation efficiencies for sodium sulfite solutions ranged up to 80%; depending on the operating conditions. The fritted-glass disperser gave recovery efficiencies of nitrogen dioxide as high as 90% from air containing 10% of the gas. The recovery efficiency decreased at low concentrations of nitrogen dioxide for both the Venturi atomizer and the fritted-glass disperser.

21. Critchley, T. (to Johnson & Sons' Smelting Works, Ltd., England). Oxidation of nitrogen oxide fumes. U.S. Pat. 2 581 518 (Cl. 23-102) Jan. 8, 1952 (appl. in England Feb. 17, 1948).

    Pure O_2 is added to the waste gas contg. NO and the whole is scrubbed with water to remove all oxides of nitrogen. The NO is thus first oxidized to NO_2 and the latter absorbed in the scrubbing water.

22. Farbwerke Hoechst Ag. Removal of nitric oxide from cracked gas. Belg. Pat. 613 976, Aug. 16, 1962 (Ger. appl. Feb. 15, 1961); C.A. 59, 4950 e (1963).

    Hydrocarbon gases contg. 0.001-0.2 vol. % NO, 10% min. alkanes, and 0.5 min % O, preferably 0.8-1.2%, are purified by compression to 7-16 atm. at 10-40° and immediate washing with H_2O or an alk. aq. soln. of pH ≥ 7. Thus, 31.5 $m.^3$/hr. (at normal temp. and pressure) of a cracked gas contg. H 28.7, CO 15.5, CO_2 11.6, CH_4 11.7, C_2H_6 0.8, C_2H_4 16.5, C_2H_2 6.2, other unsatd. compds. 2.6, N 6.0, O 0.45, and NO 0.015 vol. % was compressed to 7.5 atm. abs. at 30° and washed with 2000 l./hr. of H_2O with a residence time of 50 sec. in the column. The NO content was reduced to 0.0135%. When the O content was increased to 1.15 vol. %, the NO content after washing was 0.0001% max. When the H_2O was replaced by a 2% aq. $KHCO_3$ soln., no NO could be detd.

23. Ganz, S.N., & Kuznetsov, I.E. Rate of absorption of nitrogen oxides in hollow columns provided with a centrifugal sprayer. Zh. Prikl. Khim. 36, 1686-1692 (1963); C.A. 60, 3414 f (1964).

    The absorption column used for this investigation was a hollow cylinder, with a centrifugal sprayer at top. Grates at top and at bottom of the cylinder rendered uniform gas distribution throughout the column.

24. Kopita, R., & Gleason, T.G. (Peabody Eng. Corp., New York, N.Y.) Wet scrubbing for boiler flue gas. Chem. Eng. Prog. 64, Jan. 1968, p. 74-78; C.A. 68, 53005 r (1968).

    A discussion and review of scrubbers which can remove SO_2, N oxides, and particulate matter in a single unit was presented and included comments on air pollution code requirements, efficiencies of actual installation, construction materials, flow cycles, and savings effected with a 300,000 lb./hr. steam generator. Flow sheets are shown for removal of solids, SO_2, and N oxides with and without provision for water reuse. A wet scrubbing system can be designed to remove 99% of the fly ash from pulverized coal and stoker-fired boilers and 70-99.5% of the SO_2 in the flue gas.

25. Kramers, H., Blind, M.P.P., & Snoeck, E. (Tech. Hogeschool, Delft, Netherlands). Absorption of nitrogen tetroxide by water jets. Chem. Eng. Sci. 14, 115-125 (Jan. 1961); C.A. 55, 19372 a (1961).

    Laminar water jets of different lengths were exposed to a pure NO_2/N_2O_4 mixt. at pressures between 0.06 and 0.3 atm. The amounts of HNO_2 and HNO_3 found by chemical analysis in the liquid leaving this absorption system were interpreted in terms of absorption of N_2O_4 and its subsequent reaction. The manner in which these N_2O_4 absorption rates depend on the partial pressure of N_2O_4 and the jet length strongly support the working hypothesis that N_2O_4 is preferentially absorbed under simultaneous reaction with water according to fairly rapid first order rate formula.

26. Peters, M.S. (Univ. of Ill.) Stop pollution by nitrogen oxides. Chem. Eng. 62, No. 5, 197-200 (1955).

    Data on removal efficiency of N oxides in gases by water and by silica gel are given. When water was used as absorbent, data are obtained from spray tower, one-tray bubble-cap column, packed column, and one-stage fritter-glass-plate diffuser. The N oxide content in the gas range from 0.2 to 1.9 vol. % calcd. on a mixt. of $NO_2 + 2N_2O_4$. High efficiency (48% removal with a gas contg. 1.9% N oxides) is obtained with the fritted glass diffuser. Removal efficiency is below 32% in all other cases within the range of N oxide concens. tested. The adsorption efficiency of nitrogen oxides on silica gel is comparable to absorption efficiency of the bubble-cap column.

27. Peters, M.S., Holman, J.L. (Univ. of Ill.) Vapor- and liquid-phase reactions between nitrogen dioxide and water. Ind. Eng. Chem. 47, 2536-9 (Dec. 1955).

    The results of exptl. work have indicated that both gas-phase and liquid-phase reactions occur in the removal of NO_2 from gases by contact with aq. solns. The major part of these reactions does not occur in the bulk phases, but takes place in the gas film and the liquid film at the boundaries between the two phases. The presence of NO in the exit gas, and the increase in temp. in the absorption column indicate the existence of the gas-phase reaction. The occurrence of liquid-phase reaction is indicated by the fact the rate of removal of N oxides from a dilute gaseous mixt. is not directly proportional to the partial pressure of the water vapor at constant conditions of temp., gas rate, and gas composition. The rate of absorption of N oxides by aq. NaOH solns. decreases significantly as the temp. is raised.

28. Peters, M.S., Ross, C.P., & Klein, J.E. (Univ. of Ill.) Controlling mechanism in the aqueous absorption of nitrogen oxides in water. A.I.Ch.E. Journal 1, 105-111 (March 1955).

The reactions involved in the removal of nitrogen oxides from gases by reaction with water are reversible and proceed at a finite rate. It is possible therefore that the over-all process is controlled by the rate of the chemical reactions. On this basis an analysis of the process has been developed by the application of chemical kinetics, with consideration of reactions involving both nitrogen dioxide and dinitrogen tetroxide. The resulting differential equation has been simplified and integrated to give a final equation which can be tested experimentally. Theoretical methods are presented for predicting the extent of absorption of nitrogen oxides at various gas rates and concentrations and are compared with the experimental results. The paper presents some new concepts of the factors which control the rate of absorption of nitrogen dioxide and dinitrogen tetroxide in water. An understanding of the controlling factors in the process should indicate methods for improving the design of absorption towers in nitric acid plants and aid in the design of scrubbers for removing nitrogen oxides from waste gases.

29. Zhavoronkov, N. M., & Martynov, Yu. M. The kinetics of the absorption of nitrogen oxides by water and aqueous solutions of nitric acid. Khim. Prom. 1959, p. 150-5; C.A. 58, 5099 a (1963).

The rate of absorption (R) of NO_2 in water or dil. HNO_3 was investigated with respect to the linear gas velocity v (0.3 to 5.0 m./sec.) and the NO_2 concn. C (%) in a mixt. of N oxides. R in water is lower for low C and drops with rising temp. (expts. at 20 and 50°), but is independent of v. At higher C, R also depends on v. The N oxides are sol. in HNO_3; dissolved NO_2 can be readily displaced by N_2; at v_{N_2} = 1 m./sec. at 20°, calcd. with respect to NO_2, 0.012 vol. % of HNO_3 is desorbed into the gas phase. With excess NO_2, NO_2 goes mostly into soln.; with excess NO it is mostly NO + NO_2 and N_2O_3 that go into soln. The absorption of N_2O_3 in water or alkali soln. is directly proportional to the concn. of the equimolar mixt. NO + NO_2.

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30. Apakhov, I. A., Bulycheva, L. I., Shchelkunova, N. V., & Ershova, K. N. Effect of sulfuric acid mist on the absorption of nitrogen oxides. Khim. Prom. 42, 684-5 (1966); C. A. 65, 19735 E (1966).

This effect was examined by passing the flue gas, after the absorber with H_2SO_4-H_2O, successively through 2 lab. electrostatic filters at a rate of 1 l. /min. using 500-1000 l. /expt. Usually 95-99% of the mist was captured in the 1st filter. In other expts., the stream was passed through a centrifugal separator at a rate of 8 l. /min. and 900-1800 l. /expt. In the filter process, the sepn. of the mist permits the formation of N oxides in the filter, while in the 2nd this is not possible. Two samples of the condensate from the 1st filter were analyzed; to one, concd. H_2SO_4 and free N oxides were added and the N_2O_3 was detd. colorimetrically. The 2nd sample was dild. with H_2O and its H_2SO_4 content detd. It was assumed that during the diln., the N oxides are completely expelled. The condensate from the centrifuge was also analyzed. The amount of N_2O_3 in the mist corresponds to its content in the gas, approx. 10 mg. /m.^{3}. The majority of the N_2O_3 from the gas passes into the mist and is not absorbed by the sprayed acid. Probably the N oxides cause the mist formation.

31. Ioshpa, I. E., & Belkin, A. A. Kinetics of nitrogen absorption by sulfuric acid-nitric acid mixtures. Zh. Prikl. Khim. 40 187-9 (1967); C. A. 66, 96884 c (1967).

The conditions for satn. of nitrose by nitrosylsulfuric acid and HNO_3 and for the degree of NO_2 absorption for a single scrubbing of gas contg. NO_2 by nitrose were studied. Expts. were made on a lab. column, internal diam. 4.5/6.5 mm., length 10-16 mm., and total height of packing 2.55 m. Measurements were made at 30, 40, and 45° and for a gas-liquid vol. ratio 700-750 l. /l. The absorption-rate coeffs. calcd. from measurements at 30° (mean value approx. 5 g. /m.^{2} hr. torr.) agree with the mean value of the absorption-rate coeffs. obtained in the study of the absorption process in a flow system. Temp. rise from 30 to 40° has little influence on the value of the absorption-rate coeff. and on the degree of satn. of the soln. with nitrosyl-sulfuric acid and HNO_3. The increase of temp. has, however, a significant effect on the concn. of NO_2 in the outlet gas. (Temp. rise from 30 to 40° approx. doubles the concen. of NO_2 in the outlet gas.) Concn. of NO_2 in the inlet gas affects considerably the compn. of nitrose. For a doubled scrubbing rate at 40°, the concn. of NO_2 in the outlet gas is diminished approx. to 1/3 and the absorption-rate coeff. is increased approx. 1.6 times. At the same time the percentage of N_2O_3 and of HNO_3 in the outflowing nitrose is decreased.

32. Ioshpa, I. E., & Krivonogov, V.P. Determination of scale-up factor from laboratory to industrial packing in absorption of nitrogen dioxide by sulfuric acid-nitric acid mixtures. Zh. Prikl. Khim. 40, 189-190 (1967); C.A. 66, 96885 d (1967).

The kinetics of absorption of NH_3 by H_2O was studied on the same lab. equipment and under the same hydrodynamic conditionsas the absorption of NO_2 by nitrose (cf. preceding abstr.) The column was packed with glass rings, 4.5/6.5 mm. diams., av. length 13 mm., and sp. packing surface 829 $m.^2/m^3$. The measured absorption-rate coeff. of NH_3 by H_2O was 93.3 kg. moles/$m.^3$ hr. atm. The value of the absorption rate coeff. of NH_3, by H_2O on industrial Raschig rings 25x25x3 mm., is 81.8 kg. moles/$m.^3$ hr. atm. is calcd. from the formula $K = 0.076 W_g^{0.57} W_l^{0.41}$, where W_g and W_l are superficial mass velocities of gas and liquid, resp. From absorption-rate coeffs. of NH_3 by H_2O on lab. and industrial packing it follows that, in the case of absorption of NO_2 by nitrose, the lab. absorption-rate coeff. must be reduced by a factor of 1.14 when applied to industrial Raschig rings 25x25x3 mm packing.

33. Kuz'minykh, I.N., & Surkov, E.I. Bubble tower for removing nitrogen oxides from gases with sulfuric acid. Khim. Nauka: Prom. 2, 523-4 (1957); C.A. 52 4939 d (1958).

Absorption of nitrogen oxides (0.5-0.6%) at the end of a production line with H_2SO_4 in a bubble tower (1300 mm. high) was investigated. Steel plates (5) 5 mm. thick with 3 mm. perforations 5.5 mm. apart were placed 200 mm. above each other. With 40-mm. depth the degree of absorption α on 1 plate was 50% with a liquor rate of 4 cu. m. /m. hr. and a gas rate 1.2 m. /sec. with 89-91% H_2SO_4 at 50°. On 5 plates α was 95%. To reduce a tail gas of 0.2-0.3% nitrogen oxides to the tolerance concn. of 0.05-0.06% 3 plates were sufficeint (α= 80-5%); the back pressure was 150 mm. H_2O. In the range of 75-8% H_2SO_4 the effect of the acid concn. on the coeff. of mass transfer K was the highest, ± 20%; increasing the concn. from 78 to 89% did not affect α; the nitroso concn. of the acid did not affect K.

34. Lentia GmbH. (Schmidt, A., Weinrotter, F., & Mueller, W., inventors). Separation of nitrogen oxides from gases. Ger. Pat. 1 204 640 (Cl C 01b) Nov. 11, 1965 (appl. Feb. 12, 1964); C.A. 64, 4661 f (1966).

The sepn. of N oxides from gases where the mol. NO concn. exceeds the NO_2 concn. is described. An absorption system with 2 Raschig-ring packed columns, each of 100-mm. diam. and a height of 800 mm., was used. In the 1st step, the gas is treated with 96% H_2SO_4 and 45% HNO_3 sufficient for the conversion of NO to N_2O_3. In a 2nd step, the

34. Cont'd. N_2O_3 is converted to HSO_5N by concd. H_2SO_4. Thus, e.g. 10 m.^{3}/hr. of a gas contg. 6 g. N/m.^{3}, 1.2 g. as NO_2, was entered at the bottom of the 1st column, passed through the column, and was then fed to the 2nd column. The H_2SO_4 (2 kg./hr.) entered the top of the 2nd column and was recycled, the excess being fed to the top of the 1st column. The excess acid from the 2nd column was mixed with 200 g. 45% HNO_3/hr. and fed to the top of the 1st column. In the 1st column, the N concn. was decreased to 2.4 g./m.^{3} and in the 2nd to 0.6 g./m.^{3} The excess acid from the bottom of the 1st column was recovered as HSO_5N, the remainder being recycled.

35. Safiullin, N. Sh., & Tseitlin, A.N. Absorption of nitrogen oxides in sulfuric acid. Zh. Prikl. Khim. 36, 490-5 (Mar. 1963); C.A. 59, 1308 b (1963).

Absorption of N oxides from a gas contg. o.15-0.20% NO by 76-98% H_2SO_4 was studied in a packed column at 18-20°. The rate of absorption const., K, increased rapidly with the concn. of H_2SO_4 in the 76-85% range. Above this concn. K approached constancy. As a function of the gas velocity, w, $\log K = bw^n$, for w = 0.4-0.8 m./sec., n = 0.17. As a function of the liquid rate, V, $K = bV^c$. In the V ranges of 2.9-5.8 and 5.8-11.6 cu. m./sq. m., c = 0.45 and 0.085, resp. Increasing the HNO_3 concn. in H_2SO_4 from 0 to 4.4% lowered K by 8%. As a function of the temp., K = bt- N; up to 40°, N = 0.915 and at 40-60°, N = 0.545.

36. Stopperka, K., & Kitz, F. (Tech. Univ., Dresden, East Germany). System H_2O-SO_3-N_2O_3. I. System H_2SO_4-H_2O-N_2O_3. Z. Anorg. Allg. Chem. 348, 58-70 (1966); C.A. 66, 41121 w (1967).

The system H_2SO_4-H_2O-N_2O_3 was investigated. The amt. of N_2O_3 absorbed in 50-100% H_2SO_4 at 19, 60, and 95° is directly proportional to the acid concn. and inversely proportional to the temp. The NO+ formation according to the equating $2H_3O^+ + N_2O_3 \rightleftharpoons 2NO^+ + 3H_2O$ occurs only at H_2SO_4 concns. < 52%. Absorption in highly concd. H_2SO_4 results in the formation of cryst. $NOHSO_4$. The ir spectra are given for N_2O_3 in H_2SO_4. Data on x-ray interferences of $NOHSO_4$ are tabulated.

37. Tseitlin, A.N., & Romanenko, K.E. Nitrogen oxide absorption by sulfuric acid. Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Teklnol 9 (1) 85-88 (1966); C.A. 65, 6770 c (1966).

The absorption of N oxides from air contg. about 10% N oxides (50% oxidized) by 78-95% H_2SO_4 contg. 0.78% N_2O_3 was studied in a 2-cm. diam. wetted-wall column having a surface area of 0.0138 m.^{2}. With an absorbent flow of 50 ml/min. at 30°, the coeff. of absorption K, g./m.^{2} hr. mm. Hg, increased from 20 at 0.2 m./sec. gas flow to 70-110 at 1.0 m./sec. and increased only a little more as gas flow was increased to 2.0 m./sec. In tests at 50°, liquid flow variations from 50-150 ml./min. had little effect on K. At 50° with 75 ml./min.

37. Contd. absorbent, K increased sharply as H_2SO_4 concn. increased from 78 to 85% but little further increase in K was noted with 95% acid. With 78% H_2SO_4, increase in N_2O_3 concn. in H_2SO_4, and increases in temp. (in the range 30-70°). resulted in decreased K.

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38. Pauling, H. Removal of nitrogen oxides. Ital. Pat. 683 704 (Cl. C 01 b) Feb. 27, 1965 (Ger. appl. Apr. 20, 1961); C. A. 65, 3394 a (1966).

N oxides which form, e. g., during the prepn. of HNO_3, are safely removed by oxidn. to N_2O_3, followed by washing with 3 wt. % NH_4NO_2, formed by the addn. of gaseous or aq. NH_3, cooling the soln. to ~30°, and then heating in the presence of H_2O and N to remove the oxide through the decompn. of the ammoniacal soln. $NaNO_2$ and excess NH_3 are used to remove the last traces of the N oxides through the formation of decomposable ammonium salts. Descriptions of the washing technique and app. used are given.

39. Varlamov, M. L., Manakin, G. A., & Zbrozhek, L. S. Use of liquors formed during the ammonia method of purifying waste gases from nitrose sulfuric acid systems as fertilizers. Khim. Tekhnol., Respub. Mezhvedon. Nauch.-Tekh. Sb. 1967, No. 7, 21-25; C. A. 69, 18316 s (1968).

All of the acidic components in the waste gases from the nitrose sulfuric acid plants could be absorbed in an ammoniacal scrubbing liquor. The spent liquor contains N values, such as NH_3, NO_3^- and NO_2^-, up to 10% by wt. (80% as NH_3 and 20% as N oxides). It is estimated that from a nitrose H_2SO_4 plant with a capacity of 500 ton/day, the spent scrubbing liquor could amount to 22,800 tons/yr. This liquor could be utilized in the manuf. of fertilizers.

40. Pawlikowski, S., Aniol, S., & Bistron, S. Absorption of nitrogen oxides in aqueous ammonia in nozzles. Przemysl Chem. (Warsaw) 42, 490-4 (1963); C. A. 60, 6501 e (1964).

The process was conducted in a closed conical app., fitted with a device for spraying aq. NH_4OH or aq. NH_4HCO_3. The product (NH_4NO_2 + NH_4NO_3) was continuously removed and a slight excess of NH_4OH, maintained throughout the process, ensured its stability. The expts. were performed with N oxides of different compn. and

40. Cont'd. concn. The 24-hr. capacity of the app. was 1 ton of NH_4 salts, calcd. as NH_4NO_2, with an inlet concn. of N oxides of 9.0% and nominal absorption efficeincy of 65%. An increase in NO_2 concn. from 0.31 to 7.93% in the inlet gas caused the following: a decrease in absorption capacity of the reactor from 100 to 78.0%, in N efficiency of the process from 70.5 to 54.0% and an increase in 24-hr. capacity from 22.8 to 508 kg. NH_4NO_2, in temp. from 4 to 43.5°, in the vol. absorption coeff. from 0.33 to 7.38 kg. N/cu. m. hr. The absorption efficiency of N oxides in the app. was very low.

41. Streight, H.R.L. (du Pont Co. Canada Ltd., Kingston). Reduction of oxides of nitrogen in vent gases. Can. J. Chem. Eng. 36, 3-11 (1958); C.A. 52 6731 h (1958).

NO and NO_2 in the effluent gases from HNO_3 and nylon intermediate manuf. were reduced by absorption in a waste caustic NH_3 liquor. Finely dispersed NH_3 salts were removed by a venturi scrubber. Pilot-plant and full-scale operating data are given.

42. Varlamov, M.L., & Kordon, I.V. Optimization of the process of trapping low concentrations of nitrogen oxides by the ammonia method in a foam column. Zavodsk, Lab. 32 (3), 324-6 (1966); C.A. 64, 18979 d (1966).

For obtaining a math. model of the process taking place in the absorption column, the method of multifactor planning of the expt. was used. The independent variables were: x_1 consumption of NH_3 (in 1.) in the form of HN_4OH with respect to the entering N oxides (in 1.), $NH_3/(NO + NO_2)$; x_2 consumption of liquors for irrigation of the app., 1/hr.; x_3 concn. of N oxides (NO and NO_2) in the gas, vol. %; x_4 pH of the irrigating soln,; x_5 volumetric gas rate, m.^{3}/hr.; and x_6 concn. of salts in the circulating liquors, wt. %. The output parameter y characterized the degree of absorption of N oxides in the app., in %. The degree of oxidn. of NO was taken as const. and equal to 0.6, and the temp. was held at 20 ± 3° during the expts. The following regression equation was obtained: $y = 47.01 + 2.78x_1 - 1.29x_2 + 3.23x_3 + 1.55x_4 + 1.35x_5 - 4.9x_6$. The method of steepest ascent with respect to a nominal gradient was used for detg. the optimum conditions of absorption. From the results of the above method, a planning matrix was constructed and the regression coeffs. were calcd.

43. Varlamov, M.L., Manakin, G.A., & Zbrozhek, L.S. The use of sieve plate apparatus for the removal of the oxides of nitrogen from waste gases of the tower sulfuric acid system. Nauchn. Zap., Odessk. Politekhn. Inst. 32, 57-67 (1961); C.A. 59, 7171 h (1963).

43. Cont'd. Using a sieve-plate absorption column and an NH_3 solution as scrubbing liquor, about 90% of the nitrogen oxides in the waste gas was removed. The effluent from the scrubber contained 0.03% nitrogen.

44. Varlamov, M.L., Manakin, G.A., Zbrozhek, L.S., & Starosel'skii, Ya. I. Study of ammonia method for the removal of nitrogen oxides from waste gases from towers of the nitroso-sulfuric acid system. Zh. Prikl. Shim. 36, 2335-2343 (1963); C.A. 60, 6513 f (1964);

The scrubbing of N oxides from the stacks of the chamber acid process with aq. NH_4OH was studied in a pilot plant with packed columns. With a liquor rate of 11-20 cu. m./cu. m. hr. of 0.74-1.97% NH_4OH the degree of purification, α, from a gas contg. 0.379% acid gases was 74.3-77.4%. The exit gases contained 0.0764% ($NO + NO_2 + 2SO_2$). Increasing NH_4OH from 1 to 1.67% did not affect α. In a foam app. with a capacity of 20 cu. m./hr. gas, $\alpha = 90\%$, reducing the content of N oxides to 0.03% which is below the max. amt. according to sanitary requirements.

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45. Badische Anilin-& Soda-Fabrik Ag. (Nonnenmacher, H., & Kartte, K., inventors.) Selective elimination of nitrogen oxides in oxygenated gaseous mistures. Belg. Pat. 655 115, Apr. 30, 1965 (Ger. appl. Oct. 31, 1963); C.A. 64, 19033 d (1966).

When HNO_3 is manufd., it is necessary to eliminate the NO and NO_2 produced by the reaction. An improved method using V, Mo, and W oxides as catalysts, eliminates the high consumption of combustibles and the loss of catalyst activity. These oxides are used in combination with Al_2O_3 or H_2SiO_3 in a proportion of 2-50 wt. % oxides. By this procedure, a very selective elimination of N oxides is effected, without extg. O_2 at the same time; moreover, the fraction of NO_2 in the gas mixt. has no deleterious effect on the catalysts and hence, does not shorten their lives. The V oxide catalysts are not senstivie to S. The residual gases, which are formed during the prepn. of HNO_3 from NH_3 or generated during nitration procedures, usually contain 0-15 O_2, 0-2 NO, and 0-2 vol. % NO_2, the rest being inert gases such as N_2; the mixts. may also contain up to 5% H_2O vapor. The quantity of NH_3 desirable for a selective elimination ($>90\%$) of N oxides is 1-1 1/2 times the N oxide content. The gas mixt. contg. NH_3 is passed over the catalyst at a rate of 10,000-30,000 vols./catalyst vol./hr. The gas is introduced at 200-350° and the pressure varies between 1-20 atm. For example, a gas mixt. contg. 96.1 N, 3.5 O, and 0.43% NO, mixed with 0.86% NH_3 (3 times the equiv. of NO) is passed at 200° over a catalyst of 8.9% V_2O_5 with H_2SiO_3 at a rate of 10,000 vols./catalyst vol./hr. The gas leaving the catalyst contains 0.09% N oxides (79% of the oxides eliminated.) When the temp. is raised to 270°, this is raised to 91.4%. If H_2SiO_3 only is used, only 16.5% is eliminated.

46. Cohn, J.G.E., Steele, D.R., & Anderson, H.C. (to Engelhard Inds., Inc.) Removing oxides of nitrogen. U.S. Pat. 2 975 025, Mar. 14, 1961.

NO and/or NO_2 in gases may be eliminated by adding NH_3 and passing the mixt. through a Pt or Pd catalyst bed at 200°-300° and 1-4 atm., at a space velocity of 17,000-86,000 per h. The reaction: $2NH_3 + 3NO = 2.5N_2 + 3H_2O$.

47. Engelhard, Inds. Inc. (Keith, C.D., & Kenah, P.M., inventors.) Catalytic purification of gases containing nitrogen oxides and catalyst therefor. Fr. Pat. 1 365 787 (Cl. C 01b) July 3, 1964, (U.S. Appl. Aug. 14, 1962); C.A. 62. 10111 e (1965).

N oxides are removed from gases by treating a mixt. of these gases with NH_3 on an appropriate catalyst at 150-400° and spatial speed 3,000-100,000 vol. of mixed gases per catalyst vol. per hr. The catalyst is a Pt-group metal deposited on partially fritter Al_2O_3. The Al_2O_3 has a specific surface of 10-100 m.^{2}/g., is mainly k phase, which crystd. at 500-900° C. In an example, 0.3% NH_3 by vol. is added to gases contg. $\sim$ 0.2% NO + NO_2, 3-14% O, 5-6% N_2O, 2-3% CO + CO_2, the remainder, including N, being inert. This mixt. is passed over the catalyst at 220-300° and at $\sim$22,000 vols./hr. More than 90% of the NO + NO_2 is eliminated. The catalyst is prepd. by fritting or calcining classical activated 3.2-mm. Al_2O_3 rods with 0.5% Pt at 900° for 3 hrs. This catalyst can be used with satisfactory results for about $6^1/2$ months.

48. Hibernia-Chemie GmbH, & Pauling, H. Complete removal of nitrogen oxides. Neth. Pat. Appl. 6 606 577 (Cl. C 01c) Nov. 21, 1966 (Ger. appl. May 18, 1965); C.A. 66, 67453 f (1967).

N oxides were removed from waste gases by treatment with NH_3. NH_4NO_3 is formed and can be recovered. The degree of oxidn. of the N oxides was 1st increased by mixing with NO or NO_2, or gases contg. them, or by further oxidn. of the oxides to a NO_2: NO ratio of 1:1. This gas mixt. was then treated with an ammoniacal NH_4NO_3 soln. The ratio of H_2O: NH_3 in the vapor phase was limited to 2:1 for the upper range, and 100:1 for the lower range.

49. Varlamov, M.L., & Kordon, I.V. Study of the ammonia method for purifying exhaust gases of nitrogen oxides by using multifacotrial experiment planning. Dokl. Vses. Soveshch. Plan. Eksp., 1st, Moskow, 1964, 251-260; C.A. 66, 96889 h (1967); cf. ref. 42 above.

Multifactorial planning was used to obtain a math. model of this process. The main factors in the 1st foam absorption app. are the flow rates of NH_3 and of the alk. spray liquid, the concn. of NO + NO_2 in the gas, the gas rate, and the salt concn. in the recirculated spray liquid. A series of random factorial expts. was carried out to derive the yield equation as a function of these factors.

50. Ammoniaque Synthetique et Derives, S. A. Absorption of nitrogen oxides from the tail gases in the manufacture of nitric acid. Belg. Pat. 412 314, Dec. 31, 1935; C.A. 30, 5735 (5) (1936).

The N oxides are absorbed by an alk. soln. or by an alk. earth suspension which is atomized by the impact of the gases contg. the oxides to be recovered.

51. Ganz, S.N. Increased removal of nitrogen oxides from exit gases by alkaline absorption. Izv. Vysshikh Uchebn. Zvedenii Khim. i Khim. Teknol. 4, 998-1002 (1961); C. A. 56, 15322 b (1962).

Exptl. work indicated that a better absorption of N oxides from exhaust gases by alkaline solns. may be achieved by feeding a small amount of conc. NO_2 gas into the exhaust gas before the latter is passed through the absorption column, which then absorbs 80-85% of the total N oxides in the exhaust gas.

52. Grosspietsch, H., & Kalfenhauser, H., & Heuse, O. (to Farbwerke Hoechst AG). Removing nitric oxide from gases containing unsaturated hydrocarbons. U.S. Pat. 3 192 009 (Cl. 23-3) June 29, 1965 (appl. Jan. 31, 1962).

Gases contg. o. 001-0. 2% NO and more than 10% unsaturated hydrocarbons are mixed with enough air to give an O_2 content of at least 0. 5%. If that much O_2 is already present in the gases, no air needs to be added. The gases are then compressed to 2-50 atm. Under these conditions all of the NO is converted to NO_2 and N_2O_4. The compressed gases are then scrubbed with an aqueous alkaline or neutral solution at 0^o-30^o and under 2-50 atm. pressure to remove NO_2 and N_2O_4.

53. Kuz'minykh, I.N., Aigina, E.P., & Babushkina, M.C. Absorption of nitrogen oxides by soda and lime solutions. Khim. Prom. 1953, No. 8, p. 26-27; C.A. 52, 5094 g (1958).

The absorption of NO and NO_2 (by soda solns. and lime water) when bubbled through a single orifice was studied. The greatest degree of absorption occurs at a ratio NO_2:NO = 1:1, at a high concn. of N oxides in the gas and low temp. The lime water is a better absorbent than is the soda soln. Increase in the soda soln. concn. improves the absorption of the N oxides; its neutralization decreases absorption. The lime soln. concn. has relatively little effect on the absorption. With the increase of the satn. with $Ca(NO_2)_2$ the degree of absorption is lowered. Increase in the bubbling depth over 30 mm. causes very slight increase of the absorption.

54. Mirev, D., Balarev, K., Boyadzhiev, L., & Lambiev, D. Absorption of nitrogen oxides by vibrating layers of NaOH solutions. Compt. Rend. Acad. Bulgare Sci. 14, 259-262 (1961) (in German); C.A. 56, 66 a (1962).

54. Cont'd. The effect of the following variables on the completeness of the absorption was studied: NO:NO_2 ratio, O_2 concn., (NO + NO_2) concn., and flow rate. The completeness of the reaction reaches a max. at a 1:1 mole ratio. At this ratio the O_2 and (NO + NO_2) concns. have no effect. At a higher ratio, an increase of the C_2 concn. favors the absorption.

55. Radhakrishna, G.N. The removal of nitrogen oxides from air-polluting exhausts. Ductorate dissertation 1965, Purdue Univ., Lafayette, Inc., 207 pp.; Dissertation Abs. 26 (2), 943-4 (1965); C.A. 63, 17025 e (1965).

The hydroxides selected for investigations included potassium, sodium and calcium hydroxides. The experiments performed on these hydroxides in dilute solutions (2 to 5% by weight) were devoted not only to an understanding of the mechanisms involved in the process of absorption of nitrogen peroxide diluted with nitrogen, but also to making a comparative study of the use of the hydroxides as absorbing agents for the gas and neutralizing agents for the acids formed in the process of absorption. The results indicated that when the alkali was in excess in solution, almost equimolar quantities of nitrite and nitrate were formed. But, after all the alkalinity was utilized for neutralizing the acids formed, the nitrites decreased and the nitrates increased in concentration considerably. For a comparative study of the use of hydroxides in dilute solutions for absorbing NO_2, it was concluded that on the basis of weight, sodium hydroxide was more efficient than calcium or potassium hydroxides. However, the ability to neutralize the acids formed, decreased in the order: caclium, sodium and potassium hydroxides. The solids selected for investigation included Ascarite, (8-20 mesh), silica gel (20-60 mesh), calcium oxide and barium oxide (20-60 mesh). The results indicated that Ascarite has a better capacity than silica gel for the removal of nitrogen peroxide at flow rates of about 36 liters per hour and in the range of concentrations of 0.79 to 1.5 mole per cent NO_2, but at lower concentrations silica gel appeared to be a better removal agent. The weights of NO_2 removed by Ascarite increased with concentrations of the gas and decreased with increasing rates of flow within the range of concentrations used (0.70 to 1.36 mole per cent), and the range of flow rates adopted 30.0 to 45.0 liters per hour). For the silica gel, the weight of NO_2 removed by adsorption increased with the partial pressures, as well as with the concentrations of NO_2 in N_2, within the range of partial pressures (0.051 to 0.496 mm. Hg.) and concentrations (0.510 to 1.503 mole per cent). The results of absorption of NO_2 by calcium and barium oxides were poor, possibly due to dry gases being used. The presence of moisture in the gases was expected to improve the removal.

56. Shelud'ko, M.K. Removal of nitrogen oxides from industrial waste gases. Khim, Teknol., Resp. Mezhvedomstyv. Nauchn.-Tekhn. Sb. 1965, (3) 76-85; C.A. 65, 20739 e (1966).

56. Cont'd. Nitrogen oxides in the waste gases are removed by absorption in alkali solutions, but in order to remove enough nitrogen oxides to meet the standards of a sanitary atm. the NO in the waste gases must be first oxidized to the extent of 60% min. This oxidation is best carried out by adding 45-49% HNO_3 to the waste gas stream. For a HNO_3 plant this treatment would require HNO_3 equivalent to 1.5% of total production.

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57. Ganz, S.N., & Kuznetsov, I.E. The rate of absorption of the oxides of nitrogen in a hollow equiflow tower with a centrifugal volume sprayer. I, II. Tr. Dnepropeler. Khim.-Tekhnol. Inst. 1963 (16) 3-26; C.A. 61, 2746 f (1964).

I. The influence of the hydrodynamic factors was studied on the rate of absorption of N oxides in a hollow tower with a centrifugal vol. sprayer. Detd. were the optimum values of the rate of rotation of the sprayer, of the liquid rate, and of the vol. rate of the gas. By comparison of the productivity of a unit of the reaction vol. of packed and hollow spraying app., it was found that the rate of the hollow tower is 4-5 times more than the packed towers. A redn. of the dimensions and of the hydraulic resistance of the hollow towers during use for absorption of N oxides allows a lowering of capital and operating expenses by 1.5-2.0 times in comparison with the packed app.
II. The influence of the phys.-chem. factors was investigated on the absorption of N oxides with solns. of Na_2CO_3 in a hollow equiflow absorber with a centrifugal volume sprayer. A major factor during absorption of the N oxides is the preliminary oxidn. of NO so that the ratio of NO to NO_2 in the gas will be $\geq$ 1:1; a small excess of NO_2 in the gas does not cause a redn. of the rate of absorption. The feasibility of effective oxidn. of NO with weak (50%) HNO_3 was shown. The greatest rate of absorption of the N oxides is observed with a concn. of Na_2CO_3 of 60-100 g./l. Variation of the Na_2CO_3 concn. in the soln. in the ranges of 3-180 g./l. and the presence in the soln. of nitrite and nitrate salts up to 250 g./l. do not cause a significant redn. of the rate of absorption. Lowering the temp. to 10-15^{o} and increasing the concn. of NO + NO_2 in the gas up to 1.2-1.5% increase the rate of absorption.

58. Ganz, S.N., & Kuznetsov, I.D. Alkaline absorption of nitrogen oxides in a hollow even-flow tower with a centrifugal space atomizer. Zhur. Prikl. Khim. 36, 1693-7 (Aug. 1963); C.A. 60, 7694 h (1964).

Absorption with a soln. contg. 110 g. Na_2CO_3/l. at liquid rate = 2.2-6 cu. m./sq. m. hr., spray velocity = 23 m./sec. at 30^{o} with a gas rate = 167 cu. m./cu. m. hr. showed that the degree of absorption, α, and the coeff. of absorption, K_g, increased with the degree of oxidn. α_0, of NO; the latter was varied from 30 to 60% by passing the gas through

58. Cont'd. 50-53% HNO_3. Oxidn. of NO in the spray column was 15-18% higher than in a packed tower. With $\alpha_O = 38-40\%$, α and K_g increased as the concn. of NO + NO_2 in the gas, C_{NO}, increased from 0.6 to 1.2%. The increase in α with C_{NO} was pronounced only at $C_{NO} < 0.6\%$. α and K_g decreased as the temp. increased from 10 to 40°. At 10°, $\alpha = 90\%$.

59. Koninklijke Nederlandsche Hoogovens en Staalfabrieken NV. (van Ommeren, B.G.H.J., inventor). Low nitric oxide-content fuel gas. Brit. Pat. 937 364 (Cl. C 106) Sept. 18, 1963 (appl. May 19, 1960); C.A. 60, 336 b (1964).

The fuel gas contg. small amounts of NO is treated with ozone under a pressure of 6 atm. to oxidized NO to NO_2. After that, the gas is scrubbed with aq. soln. of Na_2CO_3 or $NaHCO_3$ to remove NO_2.

60. Kuz'minykh, I.N., Rodionov, A.I., & Mishchenko, Yu. S. Absorption of nitric oxide from nitrogenous exhaust gases in large-scale plate columns. Tr. Mosk. Khim.-Tekhnol. Inst. 1961, No. 33, p. 43-47; C.A. 57, 2022 h (1962).

A 12 tray, 150 mm. diam. column was used to det. optimum operating conditions and the effect of the NO-NO_2 ratio in the inlet gas on atm. pressure scrubbing of 0.3% gas at room temp. with 10% Na_2CO_3 soln. With perforated trays with downcomers, between 43 and 75% of the N oxides were removed, with overall gas velocities of 1.3 m./sec., and 4.3 cu. m./sq. m. hr. liquid loading. The max. absorption (75%) was obtained for equal mole rates of NO and NO_2, and the column performance depended more on the degree of oxidn. of NO than on gas or liquid loadings, with NO to NO_2 ratios of 0.41-0.60.

61. Mirev, D., Balerev, K., Boyadzhiev, L., & Lambiev, D. Absorption in a vibrating layer. II. Absorption of nitrogen oxides in solutions of NaOH and Na_2CO_3. Izv. Inst. Obshcha Neorg. Khim., Org. Khim. Bulgar Akad. Nauk 8, 83-101 (1961); C.A. 57, 5752 h (1962).

Gases contg. small amounts of N oxides are passed through a layer of vibrating soln. of 2N KOH and/or K_2CO_3. The N oxides are absorbed completely if the oxidation of NO to NO_2 is greater than 50%. There should be enough free O_2 in the gas to insure this oxidation. Within the range of N oxides 0.55-1.8% as NO, and a space velocity up to 800 per h. The residual N oxides concn. in the exit gas is independent of initial N oxide concn.

62. Mirev, D., Balerev, K., Boyadzhiev, L., & Lambiev, D. Absorption of nitrogen oxides in a vibrating layer of sodium carbonate solutions. III. Compt. Rend. Acad, Bulgare Sci. 14, 345-8 (1961); C.A. 56, 5795 3 (1962).

62. Cont'd. The absorption of N oxides by Na_2CO_3 solns. in a vibrating layer was studied under various conditions. The expts. were made with mixts. of gases contg. 0.55-1.8% N oxides (NO and NO_2). The degree of oxidn. of NO to NO_2 (α) varied from 20 to 60%. The effect of α, O content, velocity of gas flow, absorbent concn., and temp. on the efficiency of absorption (η) was detd. from the presence of N oxides in gases after absorption. The amt. of N oxides in exit gases was considerably smaller during absorption in the vibrating layer than that obtained by the bubbling method. The efficiency of absorption by Na_2CO_3 soln. increases with decreasing temp. from $\eta = 72\%$ at 73° to $\eta = 98.5\%$ at 0°. The rate of gas flow and concn. of NO in gases affect the absorption: at a rate of 800 cu. m./cu. m. hr. the η was 87 at NO 0.55, 91.5 at NO 0.7, and 94 at NO 1.0%; at 200 cu. m./cu. m. hr., η was 96.97, and 98%, resp. The concn. of Na_2CO_3 in soln. was 2N in all expts.

63. Pawlikowski, S., Aniol, S., & Bistron, S. Experiments of NH_3 absorption of N oxides in the nozzle systems on semitechnical scale. II. Absorption by a mixture of ammonium carbonate and bicarbonate solutions. Przemysl Chem. (Warsaw) 43, 80-83 (1964); C.A. 60, 14150 b (1964).

Production of NH_4NO_2 by absorption of NO + NO_2 in the mixt. of $(NH_4)_2$-CO_3 and NH_4HCO_3 was studied in a semitech. installation of 1/10th of the size of the proposed industrial system. In the course of investigation the effect of the following parameters were examd: (1) the concn. of N oxides, (2) the excess of absorbing medium in the mixt., (3) the pressure in the absorber, (4) gas flow rate; the safety aspects were also investigated. Optimum absorption was achieved with an absorbing soln. in which the mole ratio of NH_3 to CO_2 is as low as possible, because at these conditions the heat effect is small and the temp. increases is not high enough to cause NH_4NO_2 decompn., hence high N efficiency (90-9%) and the total efficiency (70%). The increase of pressure in the reactor by 0.8 atm., higher concn. of oxides, and higher gas flow rate have a little effect on the absorption efficiency. The aspect of safety was examd. by maintaining a steady excess of N oxides in relation to alk. component of absorbing medium. The temp. in the absorber never exceeded 50° and the rate of NH_4NO_2 decompn. never attained violent proportion. The final product was 25% NH_4NO_2 soln. which solidifies at -16° and can thus be transported by pipes even at av. winter conditions.

64. Pietrek, M. Aerosol to remove nitrous gases in the atmosphere. Czech. Pat. 105 998, Dec. 15, 1962 (appl. June 8, 1961); C.A. 60, 2250 b (1964).

An aerosol prepared from 6% Na_2CO_3 and 6% $KMnO_4$ in H_2O removes noxious gases from air which may be caused by dynamite blasts.

65. Potasse et Engrais Chimiques (Quanquin B., & Trimbach, H., inventors). Purification of waste gases from complex fertilizer manufacture. Fr. Pat. 1 408 302 (Cl. C 05b) Aug. 13, 1965 (appl. July 1, 1964); C.A. 65, 5076 f (1966).

The waste gases from the fertilizer plant are first scrubbed with 15-30% H_2SiF_6 soln. at 40°-75° which removes 90-95% of the F compds. The gases are next scrubbed with aq. Na_2CO_3 or K_2CO_3 at a concn. of 3-5 g./l., or with aq. $HaHCO_3$, $KHCO_3$ of $Ca(OH)_2$. In either case the NO_2^- and/or NO_3^- in the scrubbing soln. is maintained at a total of 50-90 g./l. The scrubbed gases contain F 3-10 mg./cu.m., and N oxides 0.02-0.05 vol.%.

66. Potasse et Engrais Chimique (Quanquin, B., inventor). Nitrogen oxides recovery from gaseous effluents. Fr. Pat. 1 387 207 (Cl. C 01b) Jan. 29, 1965 (appl. Dec. 16, 1963); C.A. 62, 14210 a (1965).

The waste gas from the HNO_3 plant is scrubbed in 2 stages by aq. $KHCO_3$ solns. In the 1st stage the $KHCO_3$ is 10 g./l. and in the 2nd stage the $KHCO_3$ is 80 g./l. The 2 scrubbing columns are maintained at 40°-45°. When the KNO_3 and KNO_2 have been built up to a sufficient concn. the scrubbing solns. are withdrawn and treated with HNO_3 to oxidize all KNO_2 to KNO_3, liberating NO gas which is collected and sent back to the HNO_3 plant. The KNO_3 soln. is then cooled to 30° to crystallize KNO_3 which is recovered as a by-product.

67. Pozin, M.E., Kopylev, B.A., & Bel'chenko, G.V. The absorption of nitrogen oxides in soda solutions in the Penn apparatus for the production of sodium nitrate. Trudy Leningrad. Teknol. Inst. im. Lensoveta 36, 120-132 (1956), C.A. 52, 14106 e (1958).

In the Penn app. a mixt. of NO + NO_2 can be absorbed by a Na_2CO_3 soln. so as to form $NaNO_3$ + $NaNO_2$ with very small losses of the oxides, but the efficiency coefficient (equiv. N oxides absorbed/equiv. Na_2CO_3 used) will drop from 30 to 16% if the linear rate of gas flow is increased from 0.5 to 3 m./sec. over the total cross section of the app. The absorption coeff. increases with the linear rate of gas flow; it reaches a value of 1860 kg./sq. m.-hr.-kg./cu. m., a value which is 6-7 times as great as the value obtained in bubble-cap columns and 20-5 times the value obtained with industrial scrubbers. The coeff. of efficiency increases slightly with liquid flow rate. If the concn. of Na_2CO_3 is raised from 5 to 20%, at a linear gas flow of 1 m./sec., the efficiency coeff. drops from 26 to 16% and the absorption coeff. drops correspondingly. If the starting concn. of the N oxides in the gas is raised from 0.05 to 1.4%, then, at a linear gas flow of 1 m./sec., the efficiency coeff. is increased from 8 to 25%.

68. Pozin, M.E., Kopylev, B.A., Bel'chenko, G.V., & Tereshchenko, L. Ya. Absorption of nitrogen oxides by soda solutions under foaming conditions. Izvest. Vysshikh Ucheb. Zavedenii, Khim. i Khim. Tekhnol. 2, 803-9 (1959); C.A. 54, 7990 i (1960).

The absorption of N oxides by soda solns. under foaming conditions takes place a few times more intensively than in towers with packings. With an increase in the linear speed of the gas, W, in the whole section of the app. from 0.5 to 2.5 m./sec., the absorption of an equimol. mixt. of N oxides (with an initial concn. of about 1%) by a soda soln. on one shelf of the foam app., decreases from 36 to 18%. The absorption coeff. under these conditions increases from 800 to 1800 kg./sq. m.-hr.-kg./cu.m. With a decrease in the concn. of N oxides in the gas below 0.5-0.6%, the absorption rate is smaller, the lower the content of N oxides in the gas. The degree of absorption of an equimol. mixt. of N oxides on one shelf of the app., for a content of about 0.2%, for W from 0.5 to 1.5 m./sec., is 10-18%. An increase in the content of nitrite-nitrate salts up to 150 g./l. in the soln. for W = 0.75 m./sec., flow rate of the liquid = 3 cu.m./m.-hr., and a Na_2CO_3 content of about 5%, has practically no influence on the absorption; for a further increase in concn., i.e., up to 500 g./l., the degree of absorption decreases from 24 to 16% for an initial nitrous content of the gas of about 0.5% NO + NO_2 and o= 50%. The absorption of N oxides by Na_2CO_3 soln. is most effective when a preliminary 50% oxidn. of N oxide is carried out, when about 5% Na_2CO_3 is used, and when heat is removed by circulating lye. The degree of absorption on one shelf of the app. of N oxide, without a preliminary oxidn., for an initial concn. of 1%, is 5-10%, and depends relatively slightly on its concn. in the gas. This indicates a partial oxidn. of NO under foaming conditions in the liquid state.

69. Rabson, S.R. Development of an extraction plant for the elimination of blasting fumes. Trans. Commonwealth Min. Met. Cong. 2, 757-774 (1961); C.A. 57, 619 i (1962).

N oxides, such as NO, NO_2, N_2O_4 and N_2O_3 are removed from air by passing the air through a contact mass made of 1/8-3/8 inch vermiculite, 2 ft. deep, impregnated with a 5% soln. of Na_2CO_3 $KnMnO_4$.

70. Skrivanek, J. Absorption of nitrogen oxide gases by soda solution. Chem. průmysl 6, 404-9 (1956); C.A. 51, 9104 d (1957).

Absorption kinetics of residual gases by soda soln. was studied for the purpose of producing nitrite from the mother liquor after absorption. The exptl. results indicate that for the production of nitrate a continuous system of packed columns seems suitable. The recycled soln. in the last column should contain 3% soda, which corresponds to the highest value of the absorption coeff. For nitrite

70. Cont'd. production on the other hand the soln. withdrawn should contain only a min. of soda. Consequently for the production of nitrite a batch system seems more appropriate unless a plate column without recycling is designed.

71. Varlamov, M. L., Drobysheva, O. M. (Polytech. Inst., Odessa). Absorption of nitrogen oxides in low concentrations by sodium carbonate solutions in an apparatus of Ventrui-tube type. Izvest. Vysshikh Ucheb. Zavedenii, Khim. i Khim. Tekhnol. 3, No. 1, 146-150 (1960); C. A. 54, 21891 i (1960).

The absorption of N oxides of low concns. (0.5-3.5% NO, NO_2) by Na_2CO_3 solns. (30-199 g./l.) was investigated in an absorption app. of the Ventrui-tube type having the following dimesnions: diam. of the cylindrical throat, d_n = 6 mm., frustum of the cone with vertex angle of 25°, and the expanding conical section increasing at a const. angle of 7°. The volumetric absorption coeff. ($K_g\alpha$) increases with an increase of the linear velocity of the gas (w_g) owing to an increase in the degree of dispersion of the liquid and to the increase in the contact surface of the gas-liquid phases. The degree of absorption (η) decreases somewhat with an increase in w_g, owing to a decrease in the time of contact of the liquid-gas mixt. in the reaction space of the app. The dependence of $K_g\alpha$ on the vol. ratio of the gas and liquid can be expressed by the equation $K_g\alpha = 517,000 \text{ (gas: liquid)}^{-0.552}$. The absorption coeff. decreases with increase in the gas:liquid ratio. With increase in the gas-liquid ratio in the range of 700-4,000, the hydraulic resistance of the app. varies relatively slightly (by ~10 mm.) With decrease in the concn. of NO and NO_2 in the gas from 3.5 to 0.5%, $K_g\alpha$ decreases by 32 to 35%. With increase in the concn. of the Na_2CO_3 soln. from 30 to 198.8 g./l., $K_g\alpha$ decreases by 15-20% and η decreases, e.g., for a concn. of N oxides of 3.5%, from 43.5 to 38%. A study of the influence of the degree of oxidn. of NO in the gas mixt. on $K_g\alpha$ shows that the greatest value of $K_g\alpha$ (96,200 kg./cu. m.-hr.-atm.) is observed at 50% conversion.

72. Varlamov, M. L., & Drobysheva, O. M. Mass transfer and chemical reaction in a venturi scrubber. Zh. Prikl. Khim. 33, 2020-9 (1960); C. A. 55, 17119 i (1961).

The liquid phase mass-transfer coeff. K_La, detd. by desorption of CO_2 from aq. solns. is a linear function of the liquor rate, Q_L, ml./min., in the range 62-132.1./min. The slope, α, of the K_La vs. Q_L lines increases with the gas velocity in the throat, w_g, in the range 36.5-77.9 m./sec. $\text{Log}\,\alpha = 7.4 \times 10^{-4} w_g{}^{1.64} = p$. $K_La = (100 - 1.13 w_g) Q_L^{p}$ (1./hr.), or $Nu_L = C(Re_L - 30)^p(pr_L)^{0.5}$, where $C = 0.145 - 0.0018 w_g$. For desorption $K_L = L^{0.2}$, for a liquor velocity in the thorat w_L = 64.9 m./sec., where L is the liquor rate, cu. m./sq. m. hr. The gas-phase mass transfer coeff., K_ga, detd. by desorption of SO_2 from an aq. soln. is correlated by $K_ga = 2820w_g$ or $Nu_g = 0.36 \times 10^{-4} Re_g{}^{0.81} Pr_g{}^{0.666}$ and $Kg = 4.8w_g{}^{0.8}$. For absorption with chemical reaction, K_ga was detd. for absorption of N oxides from air by Na_2CO_3 solns.

73. Varlamov, M. L., Manakin, G. A., & Starosel'skii, Ya. I. Absorption of nitrogen oxides by soda solutions in efficient absorption apparatus of the gas lift type. Nauch. Zapiski Odessk. Politekh. Inst. 1957, 17, 37-52 (publ. 1958); C. A. 55, 10997 c (1961).

New gas-lift type app. were developed which permit, within wide limits, a change in the relation of consumption of gas and liquid, and operation with greater linear gas velocity at comparatively low hydraulic resistances in comparison with conventional equipment. The hydrodynamics and the absorption of N oxides in low concn. by solns. of Na_2CO_3 in 6 gas-lift app. were studied in relation to concn. of N oxides, consumption of gas and liquid, diam. and height of lift pipes, their cross section, and the no. of operating cycles. For optimum gas consumption with minimum hydraulic resistance, the absorption coeff. was 100 times greater than the same coeff. for packed towers. From test lab. models it was possible to design plane parallel app. of great capacity if the same equiv. diam. was used. Exptl. data were obtained of practical interest in removing N oxides from tail gases, esp. at pressures which can be used for operation of gas lift app.

74. Varlamov, M. L., & Starosel'skii, Ya. I. Absorption of nitrogen oxides by sodium carbonate solutions in a gas-lift apparatus. Zhur. Priklad. Khim. 32, 1716-1723 (Aug. 1959); C. A. 53, 20940 d (1959);

Absorption on No and NO_2 from dil. gases by Na_2CO_3 solns. in a gas-lift type of absorber was studied. The results were expressed by the following empirical relations. At a const. gas rate, V_g, the vol. coeff. of absorption $Ka = C_{NO}^{0.31}$ With V_g from 5 to 30 l. /min. and the concn. of NO + NO_2, C_{NO} = 0.35 - 1.2% and the concn. of Na_2CO_3 in the soln., C_s = 50.5 g. /l., $Ka = V_a^{0.57} C_{NO}^{0.31}$. With C_s = 87.5 g. /l. the rate of absorption $U = V_g^{0.5} C_{NO}^{1.36}$ kg. /cu. m. -hr. The degree of absorption D decreased as V_g and the gas:liquor ratio increased. Ka decreased lineraly as the temp. increased from 20 to 50°. In the liquor rate, L, range from 0.15 to 1.51. /min., $Ka = 180L^{1.25}h^{-1.94}$, where h is the depth of submersion.

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75. The Gas Light & Coke Co., et al. Removing or converting constituents of gas mixture. Brit. Pat. 496 721, Dec. 1, 1938; C. A. 33, 4004 (2) (1939).

The gas to be treated is passed in contact with the anode of an electrolytic O_2 cell to oxidize all of the N oxides SO_2 and H_2S in the gas. The electrolyte may be a soln. of NaOH.

76. Gattys, F. J. Absorption column for nitrous gases. Ger. Pat. 1 229 502 (cl. c 01b) Dec. 1, 1966 (appl. June 30, 1961); C. A. 66 47691 d (1967).

Nitrogen oxides in waste gases are recovered by oxidation followed by absorption in dilute HNO_3 in a column designed to have an oxidation chamber on each plate.

77. Gesellschaft fur Lindes Eismaschinen AG. (Karwat, E., inventor). Removal of nitric oxide from gas mixtures. Ger. Pat. 1 085 640 (Cl. 26 d) appl. Sept. 3, 1957; C. A. 56, 5638 c (1962).

$HClO_2$ or ClO_2 is added to the water or gas mixt. to be purified at pH of 7-12. After the reaction between ClO_2 and NO, the gas mixt. is washed with NaOH, or $Na_2S_2O_3$, or Na_2SO_3 solns. Thus, 50 cu. m. N contg. 0.01% Cl was passed through a saturator filled with 50 l. of a 10% aq. $NaClO_2$ soln. at 12 atm. Then this N leaving the saturator was charged with 10 l. ClO_2 and added to a stream of 10,000 cu. m. coke-oven gas with 2% CO_2 and 1 p.p.m. NO. After 2-6 sec., CO_2 was removed, and the gas was washed with $Na_2S_2O_3$; about 40 g. $NaClO_2$ was consumed.

78. Karwat, E. (to Gesellschaft fur Linde's Eismaschinen AG., Germany). Removal of nitric oxide from gas mixtures containing the same. U.S. Pat. 3 023 076 (Cl. 23-2) Feb. 27, 1962 (appl, in Germany Sept. 3, 1957).

Small amounts of NO in gases are eliminated by oxidizing it with ClO_2 freshly prepared from reacting $NaClO_2$ with Cl_2 ($2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl$). The NO is thus oxidized to NO_2, and the NO_2 is removed by scrubbing the gas with an alkali soln.

79. Karwat, E. (to Gesellschaft fur Linde's Eismaschinen AG, Germany). Removal of nitric oxide from gas mixtures containing same. U.S. Pat. 3 149 907 (Cl. 23-2) Sept. 22, 1964 (Ger. appl. Sept. 3, 1957); Ger. Pat. 1 085 640 (1960); Chem.-Ing.-Tech. 35, 863 (1963). C. A. 56, 5638 e (1962).

$HClO_2$ or ClO_2 is added to the water or gas mixt. to be purified at pH of 7-12. After the reaction between ClO_2 and NO, the gas mixt. is washed with NaOH, or $Na_2S_2O_3$, or Na_2SO_3 solns. Thus, 50 cu. m. N contg. 0.01% Cl was passed through a saturator filled with 50 l. of a 10% aq. $NaClO_2$ soln. at 12 atm. Then this N leaving the saturator was charged with 10 l. ClO_2 and added to a stream of 10,000 cu. m. coke-oven gas with 2% CO_2 and 1 p.p.m. NO. After 2-6 sec., CO_2 was removed, and the gas was washed with $Na_2S_2O_3$. The gas thus treated contained 0.025 p.p.m. NO + NO_2. About 40 g. $NaClO_2$ was consumed.

80. Koninklijke Nederlandsche Hoogovens en Staalfabrieken NV. (Guillaume, B., & van Ommeren, H. J., inventors). Low nitric oxide-content fuel gas. Brit. Pat. 937 364 (Cl. c 10b) Sept. 18, 1963 (appl. May 19, 1960); addition: Brit. Pat. 1 080 240, Aug. 23, 1967; C. A. 60, 336 b (1964); 68, 4769 j (1968).

After scrubbing with an aq. Na_2CO_3 soln., hot flue gas obtained by combustion of hydrocarbons and contg. 5-10 ppm. of SO_2 and 40-50 ppm. NO was treated with a 20% excess of the stoichiometric amt. of O_3 required for reaction with NO and SO_2. After 5 min., the NO content was 2-3 ppm. The gas contg. the NO_2 formed was scrubbed with an aq. Na_2CO_3 soln. In the manuf. of coal gas, the soln. is added to the coal gas stream prior to the scrubbing steps.

81. Morrison, M.E., Rinker, R.G., & Corcoran, W.H. (Calif. Inst. of Technol., Pasadena). Rate and mechanism of gas-phase oxidation of parts-per-million concentrations of nitric oxide. Ind. Eng.-Chem. Fundamentals 5, 175-181 (1966); C.A. 65, 80 a (1966).

Rates of the air oxidn. of ppm. concns. of HNO_3 were studied homogeneously at atm. pressure and ambient temps. in a const.-vol. batch reactor. The initial concn. of nitric oxide was varied from 2 to 75 ppm., while the O concn. ranged from 3 to 25 vol. %. The initial order of the oxidn. reaction in the absence of N dioxide is 2.00 ± 0.09 for nitric oxide and 0.97 ± 0.11 for O. From initial rate data at 26.5°, a 3rd-order rate const. of $(1.297 \pm 0.051) \times 10^4 \, (1.)^2/(g.\text{-mole})^2\text{-sec.}$ was obtained. The addn. of N dioxide increased the initial oxidn. rate, and that compd. showed an autocatalytic effect throughout the course of the reaction. A nonlinear least-sqs. analysis was used to develop a mechanism involving 6 reactions, with NO_3, N_2O_3, and N_2O_5 as intermediates. Use of that mechanism gave a min. standard deviation of 1.6 ppm. for the predicted concns. of nitric oxide relative to the exptl. data.

82. Peters, M.S., Ross, C.P., & Anderson, L.B. (Univ. of Illinois, Urbana). Removal of nitrogen oxides from gaseous mixtures. U.S. Atomic Energy Comm. report COO-1011, Sept. 30, 1953, 99 pp.

p. 23-24. Nitrogen oxides, such as NO, NO_2, N_2O_4, and N_2O_3, may be removed quantitatively from gas mixtures by oxidizing agents in aqueous media, of the chemical reactions involved are the following:

(1) $2NO + 3\,H_2O_2 = 2HNO_3 + 2H_2O$

(2) $2NO_2$ (or N_2O_4) $+ H_2O_2 = 2HNO_3$

(3) $10NO + 6KMnO_4 + 9H_2SO_4 = 10HNO_3 + 3K_2SO_4 + 6MnSO_4 + 8H_2O$

(4) $10NO_2 + 2KMnO_4 + 3H_2SO_4 + 2H_2O = 10HNO_3 + K_2SO_4 + 2MnSO_4$

83. Ganz, S.N., Luklyanitsa, A.I., & Bel'china, L.A. (Khim,-Tekhnol. Inst. Dnepropetrovsk). Production of nitrogen-iron fertilizers from waste pickling solutions II. Zh. Prikl. Khim. 37, 1609-1611 (1964); C.A. 61, 9193 a (1964).

Spent pickling liquor contg. 25% $FeSO_4$ and 4-5% free H_2SO_4 was used to scrub a gas contg. small amounts of NO and NO_2. The apparatus was a packed column which was maintained at 20°-22°. The scrubbing solution was then withdrawn and heated to 90-100° to liberate the NO which is sent back to the HNO_3 plant. The soln. is finally treated with NH_3 to produce a N-Fe-contg. fertilizer.

84. Ganz, S.N., & Mamon, L.I. Kinetics of absorption of nitric oxide by solutions of ferrous sulfate in a mechanical absorber with a high number of revolutions. Zh. Prikl. Khim. 30, 553-561 (1957); C.A. 51, 13534 h (1957); 53, 4873 e (1959).

The rate of absorption q of NO by aq. solns. of $FeSO_4$ in a revolving app. was studied. The over-all coeff. of absorption K_v was a function of the r.p.m., n, or the peripheral velocity v_d of the disks up to a crit. value of n = 3000 r.p.m. or v_d = 6.5 m./sec. at which point K_v passed through a max. and then decreased (max. K_v = 1050 kg./cu.m hr. atm.) The decrease was attributed to the centrifugal force or to the destruction of the structure of the foam at high velocities. Up to the crit. value of v_d, log K_v vs. v_d was a linear function expressed by $K_v = 276 v_d^{0.82}$, and K_v was independent of the partial pressure P of NO and the concn. of $FeSO_4$. q was proportional to P, so that $q = K_v \Delta P_{av}$. Log K_w was a linear function of the vol. velocity of the gas up to w $\sim$1000 cu. m./cu. m. hr. In the range of linearairty $K_w = Aw^{0.86}$; the values of A for v_d 2.05, 6.28, and 10.25 m./sec. were 2.57, 5.3, and 3.89, resp.

85. Pozin, M. E., Tarate, E. Ya., Zubov, V.V., & Tereshchenko, L. Ya. (Technol. Inst., Leningrad). Velocity and mechanism of adsorption of nitric oxide by aqueous salt solutions. Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol. 6 974-981 (1963); C.A. 60, 1529 e (1964).

The process of absorption of NO by Na_2SO_3, $(NH_4)_2SO_3$, $FeSO_4$, and $FeCL_2$ solns. was studied under conditions not complicated by turbulent mass transfer, using an essentially static gas phase in contact with a mildly agitated liquid phase. Two regions of absorption of NO by sulfite solns. were observed. With low NO concn. (<0.1 bar), the absorption rate is wholly controlled by the gas phase and is described by $V = K_1P$, kg./m.^{2} hr., where P = partial pressure of NO and K_1 is the mass-transfer coeff. With NO concn. > 0.1 bar, driving force is detd. by both gas and liquid phases and absorption velocity is described by $V = K_1(P - P_i)$, where P_i = equil. pressure of NO at the boundary

85. Cont'd. layer of the liquid. Analogously there are 3 regions of absorption of NO by solns. of bivalent Fe salts, but driving force is also modified by the equil.: $k = [FeNO^{++}] / [Fe^{++}][NO]$. If the degree of satn. of the initial soln., $x = [FeNO^{++}] / [Fe^{++}]$, then a cor. partial pressure is defined by: $P^* = x/k.H(1 - x)$, where H = Henry's Law const., $V = k(P - P^* - P_i)$.

86. Pozin, M.E., Zubov, V.V., Tereshchenko, L. Ya., Tarat, E. Ya., & Ponomarev, Yu. L. Solubility of nitric oxide in aqueous solutions of some salts. Khim. i Khim. Tekhnol. b, 608-616 (1963); C.A. 60, 4870 d (1964); English transl. Chemico TR-377.

The soly. of NO in aq. solns. of $CuSO_4$, $CuCl_2$, $MnSO_4$, H_3PO_4, $CoSO_4$, $NiSO_4$, $Cu_2(NH_3)_nCl_2$, Na_2SO_3, $FeSO_4$, and $FeCl_2$ was detd. Solns. of $NaSO_3$, $FeSO_4$, $FeCl_2$, and $Cu_2(NH_3)_nCl_2$ proved to be the most efficient absorbing media. Equil. conditions were investigated for NO-$FeSO_4$ and NO-$FeCl_2$ at 10-90° and equil. consts. for salt concns. (> .7M) were detd. by the equation $10 g K = 2550/T - 8.8$. The equil. pressures of NO above solns. of $FeCl_2$ and $FeSO_4$ are given.

87. Pozin, M.E., Tarat, E. Ya., Tereshchenko, L. Ya., Zubov, V.V., & Treushchenko, N.N. Kinetics of absorption of nitric oxide by aqueous salt solutions. Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol. 8 (4), 628-632 (1965); C.A. 64, 6126 a (1966).

N_2SO_3 and $FeSO_4$ solns. are practical absorbents for NO in N or Ar streams. Studies were conducted at 20° in a 5-cm. diam. x 75-cm. high tower packed with 6 x 10 x 1.3-mm. ceramic rings, and in a 4-cm. diam. foam chamber with 3-mm. orifices providing 23% free area. Data was correlated by the following equations: for the packed scrubber with Na_2SO_3 soln.: $K_s d/D_g = 1.34 \times 10^{-6} (4w_g/fgu_g)^{0.66}(4w_l/fgu_l)^{0.6} (u_g/p_gD_g)^{0.33}(u/p_1D_1)^{0.13}(l/d)^{-0.33}$; for the foam chamber with Na_2SO_3 soln.: $K_v w_g/g = 2.1 \times 10^{-5}(w_g{}^3/v_g g)^{0.5}(i/v_1)^{0.33}(H/h)^{0.3}(v_g/D_g)^{0.33}$; for the foam chamber with $FeSO_4$ soln.: $K_v w_g/g = 2.54 \times 10^{-5}(w_g{}^3/v_g g)^{0.55} (i/v_1)^{0.35}(v_g/D_g)^{0.33}$, in which K_s = absorption coeff., m./sec., d and l = equiv. diam. and height of packing; w_g and w_l = mass flow rates of gas and liquid, kg./m.^{2}-sec.; u_g and u_l = dynamic viscosity of gas and liquid, kg./sec.-m.^{2}; p_g and p_l = d. of gas and liquid, kg.-sec.-g.-m.^{4}; D_g and D_l = diffusion coeffs. of NO in gas and liquid, m.^{2}/sec.; f = sp. surface of the packing, m.^{2}/m.^{3}; K_v = vol. coeff. of absorption, (kg./m.^{3})/(sec.)(kg./m.^{3}); w_g = surface gas velocity, m./sec.; i = intensity of liquid flow, m.^{3}/sec.-sec.; v_g and v_l = kinematic viscosity of gas and liquid, m.^{2}/sec.; H = foam height, m.; h = orifice height, m.

88. Pozin, M.E., Tarat, E. Ya., Tereshchenko, L. Ya., Zuboc, V.V., & Morariu, I. (Lensovet Inst. Technol., Leningrad). Method of expressing the driving force of absorption processes. Protsessy Khim. Tekhnol., Gidrodinam., Teplo- i Massoperedacha, Akad. Nauk SSSR, Otd. Obshch. i Tekhn. Khim., Sb. S. 1965, 218-223; C.A. 65, 17734 c (1966).

88. Cont'd. The local driving force, D, of absorption is represented by the basic equation $D = p_i - p_{ei}$ where p_i is the partial pressure of component i which is being absorbed and p_{ei} is the equilibrium pressure of i at the phase boundary. This basic equation was tested by the absorption of NO in aq. soln. of $FeSO_4$. The mass transfer coeff. is a practically const. quantity that is independent of the concn. of the absorbent and the substance being absorbed.

89. Shelud'ko, M.K. Some characteristics of green vitriol solutions as an absorbent for nitrogen oxides from industrial waste products of nitric acid apparatus. Khim. Tekhnol. Resp. Mezhvedomstv. Nauchn.-Tekhn. Sb. 1965 (2), 68-71; C.A. 65, 14877 b (1966).

The use of aq. solns. of $FeSO_4$ as absorbents for N oxides in the waste gases from the HNO_3 plant was investigated. It was found that the equilibrium concn. of NO in the $FeSO_4$ soln. decreases with the partial pressure of NO in the gas phase; that working with 1% NO in the waste gas, it took about 63 cu. m. of $FeSO_4$ soln. to treat 1,000 cu. m. of waste gas. (0.16 cu. m. NO per cu. m. of $FeSO_4$ soln.) Therefore $FeSO_4$ solns. are not recommended for use with NO removal.

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90. Ges. Fur Linde's Eisenmaschinen AG. Removing nitric oxide from gases. Ger. Pat. 521 031, Oct. 15, 1929; C.A. 25, 2838 (7) (1931).

Traces of NO are removed from gases by washing them with solns. contg. lower oxides of S or the alkali salts of the corresponding acids. Since the presence of free OH ions promotes the absorption, an alk. washing liquor is preferred, and the gases should be preliminarily freed from acid constituents other than CO_2. The method is particularly useful in purifying coke-oven gases prior to sepg. constituents thereof by liquefaction, and may be put into effect in this case by adding an alkali sulfite to the alk. washing liquor used to remove CO_2.

91. Office National Industriel de l'Azote (Garlet, R., inventor). Removal of nitrogen oxides from waste gases. Fr. Pat. 1 336 212 (Cl. C 01b, C 01k) Aug. 30, 1963; U.S. Pat. 3 329 478 (Cl. 23-2) July 4, 1967 (Fr. appl. July 11, 1962); C.A. 60, 298 b (1964).

Nitrogen oxides in waste gases are removed by scrubbing the gases with an aq. solution of NH_4HSO_3 and $(NH_4)_2SO_3$ with or without free NH_3, in which the $HSO_3^-/SO_3^=$ molar ratio is in the range 0.1 to 0.4.

92. SINCAT Soc. Ind. Catanese Soc. Per. Azioni. Abatement of nitrogen oxides emission. Fr. Pat. 1 454 723 (Cl. C 01c) Oct. 7, 1966 (appl. Nov. 11, 1964); C.A. 66, 97011 c (1967).

92. Cont'd. Emission of N oxides from chem. plants was reduced by treating these with a soln. contg. sulfite or bisulfite according to the following reactions: $2NO_2 + 4SO_3^{2-} \rightleftarrows N_2 + 4SO_4^{2-}$ and $2NO + 2SO_3^{2-} \rightleftarrows N_2 + 2SO_4^{2-}$. The gas was scrubbed at room temp. with a soln. contng. either 3.8% Na_2SO_3, 4.5 K_2SO_3, 0.25 $MgSO_3$, or 3.5 $NaHSO_3$, resp. The N oxide-contg. gas (0.3-0.4% by vol. of NO and NO_2) was bubbled through the sulfite soln. at the rate of 150 l/hr. through 250 cc. of the latter. In another example, a 1.15% by vol. of N oxides equiv. to NO_2 was charged through a Venturi tube at the rate of 18,000 $m.^3$/hr. and treated with a soln. contg. 19.5% by wt. of SO_2 as an NH_4^+ salt. In both cases, the exit gas contained 0.01% N oxides by vol. and the final soln. had a pH 6.4-6.9. The $(HN_4)_2SO_4$ was concd. and recovered.

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93. Berquin, Y.F. (Potasse & Engraise Chimiques, France). The PEC company and the problem of nitrophosphates. Proc. 15th Annual Meeting, Fertilizer Industry Round Table, Nov. 10-12, 1965, p. 88-92.

The PEC company has developed a process of absorbing nitrogen oxides from the tail gas of a HNO_3 plant in a milk of lime followed by treating the pregnant milk of lime, after filtration, with 2.0-2.5 moles of H_2SO_4 per 3 moles of calcium nitrite. Thus all the $Ca(NO_2)_2$ is oxidized by H_2SO_4 to $Ca(NO_3)_2$. If more H_2SO_4 is used, e.g. 1 mole H_2SO_4 per mole of $Ca(NO_3)_2$, then HNO_3 is formed. Under this condition, after filtering off $CaSO_4$, a 10-20% HNO_3 can be obtained.

94. Ganz, S.N. (Khim.-Tekhnol. Inst. Dnepropetrovsk). Effect of hydrodynamic condition on the rate of absorption of nitrogen oxides by solutions of calcium hydroxide in a mechanical absorber on a semi-plant scale. Zh. Prikl. Khim. 30, 1311-1320 (1957); C.A. 52, 2472 i (1958).

The study made previously with a lab. unit was extended to a unit 0.88 m. diam., 1.54 m. long, and 1 cu.m. capacity with 4 perforated disks with 14 spadelike bends in each. With a gas velocity w of 400 cu.m./cu.m. of absorber/hr through a soln. contg. nitrites + nitrates 10-20, CaO 70-80 g./l., the degree of absorption α at 60-70° increased with the peripheral velocity v_g rather rapidly at first but at decreasing rates so that at $v_g = 22\text{-}23$ m./sec. $d\alpha/dv_g$ was small and at $v_g = 27\text{-}28$ m./sec. approached zero. In the range of initial gas concn. x_1 from 0.14 to 4% ($NO\text{-}NO_2$), α increased with x_1; even with a dil. gas, 0.14-0.3%, $\alpha = 70\text{-}75\%$, which was higher than could be obtained in a packed tower. By means of the method described previously (C.A. 50, 3857b), equations were found for the coeff. of absorption $K = f(x_1, v_g)$ in the v_g range of 14-30 m./sec. The generalized form of the equation was $K = m\sqrt[3]{v_g} + n$. From a series of simultaneous equations of 2 points on each curve of the functions $m(n) = f(x_1)$, the following empirical relation was obtained $K_g = (1490 - 241x^{-1})\, v_g^{0.333} + (590x_1^{-1} - 2080)$. $K = f(w)$ was empirically expressed by

94. Cont'd. K = aw + b with values of 1.9 and 2.3 for the consts. a and b, resp. The calcd. values of K agreed with the exptl. values within 1.5%. α increased linearly with the vol. of liquor in the absorber or the ratio V of vol. of liquor/vol. absorber. At V = 0.19-0.21 α passed through a max. and decreased. Best results were obtained with 4 disks spaced 0.6-0.7 disk diams. with 14-16 spades bent at 15-17°.

95. Ganz, S.N., Braginskaya, R.I., Gorodetskii, N.I., & Lokshin, M.A. Absorption of nitrogen oxides by lime milk in mechanical adsorption pilot plant installation. Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol. 5, No. 1, p. 154-9 (1962); C.A. 57, 3245 3 (1962).

An experimental industrial app. for the absorption of N oxides with aq. $Ca(OH)_2$ is described. The dependence of the degree and rate of absorption of N oxides on the concn. of the oxides in that gas, the concn. of the nitrite-nitrate salts and CaO in soln., and on the vol. flow rate of the gas and the amt. of liquid in the app. were studied. An increase in the concn. of N oxides resulted in an increase in the degree and rate of absorption; in this case, the rate of oxidn. of NO played an important role. The degree and rate of absorption of N oxides decreased with increasing concn. of the nitrite-nitrate salts in soln.; the decrease was rapid up to a concn. of 25 g./l. and slower at higher concns. A variation in the concn. of CaO in the suspended soln. did not greatly affect the degree of absorption in the absence or in the presence of small amts. of nitrite-nitrate salts; with increasing concn. of the latter above 200 g./l., an increase in the concn. of CaO increased the degree of absorption of N oxides. Practically complete absorption of equimolar amts. of $NO + NO_2$ occurred under highly turbulent conditions for a 5-7 sec. contact of the phases. An increase in the vol. rate of the gas decreased the degree of absorption. The degree of absorption of $NO + NO_2$ was greater at lower temps.

96. Ganz, S.N., & Kravchinskaya, S.B. (Khim.-Tekhnol. Inst., Dnepropetrovsk). Rate of absorption of nitrogen oxides by solutions of $Ca(OH)_2$ in a revolving absorber. Zh. Prikl. Khim. 28, 145-155 (1955); C.A. 49, 9965 h (1955); Chemico transl. TR-62.

The feasibility of a rotary (horizontal) absorber for the absorption of $NO + NO_2$ (I) by $Ca(OH)_2$ solns. (10%) was investigated by using air and NO as the initial gas and vol. of liquor equiv. to ~20-23% of the absorber vol. In an absorber of 2 1. with 5 plates 0.094 m. in diam., 30°, and a gas rate Q, of 400 cu. m./cu. m. hr., the absorption rate w increased rapidly as a function of the peripheral velocity Z, up to 3.5 m./sec.; as Z increased to above 8.9 m./sec. the rate of increase in w approached 0, becoming independent of Z as well as the concn. of I. With 0.5-1% of I. w was 99.9% at Z = 12-15 m./sec.; with 1, 3, and 4% I, w was 96.7, 97.2, and 97.4% at Z = 8-9 m./sec. In an absorber of 0.8 1. with 3 disks 0.053 m. in diam., w was 92-96% for a gas of 0.5-1% at Z = 8.3 m./sec. and Q = 400 cu. m./cu. m. hr.; even with Q = 1400, w did not fall below 80-84%. The coeff. of absorption K_g, calcd. by K_g =

96. Cont'd. $G/Vt\Delta P$, where G is the wt. of the gas absorbed (N basis), V the vol. of the absorber, t time, and ΔP is the logarithmic mean driving force (atm.), is independent of the temp. up to 40° and slightly decreases above that up to 55°. K_g decreases slightly with the concn. of $Ca(OH)_2$ (up to 13 g. /l.) and increases with the concn. of I so that the K_g vs. $Ca(OH)_2$ concn. is a family of parallel straight lines sepd. by decreasing distances as the gas concn. increases from 0.56 to 1, 3, and 4% I. From the similarity to the bubble tower the no. of disks n required is calcd. by $[100/(100 - w_1)]^n = C_1/C_2$, where w_1 is the degree of absorption by 1 disk and C_1 and C_2 are the concns. of I entering and leaving the plate. Exptl. values of w_1 are 80.6, 82.3, 84.8, 87.3, and 90.3%; for C_1 0.55, 1.02, 2.85, 4.4 and 6.2%. The max. n required is 4. It is estd. that construction cost and operating energy of a revolving absorber are 10 and 38.4% of an equiv. packed tower. The rate of absorption of N_2O_3 is higher than that of NO_2 in a revolving absorber.

97. Ganz, S.N., & Lokshin, M.A. Effect of basic physiochemical factors on the rate of absorption of nitrogen oxides by solutions of $Ca(OH)_2$ in a rapidly revolving absorber. II. Zh. Prikl. Khim. 30, 1525-1535 (1957); C.A. 52, 5103 i (1958).

The degree of absorption α of $NO + NO_2$ by solns. of $Ca(OH)_2$ in a revolving absorber (loc. cit.) decreased as the concn. C of $Ca(NO_3)_2 + Ca(NO_2)_2$ increased. Empirically, the coeff. to absorption $K_g = mC^n$, kg. /cu. m. hr. atm. For initial concns. x of $NO + NO_2$ (60% of NO oxidized) from 0.475 to 2.125%, CaO concns. from 3 to 5 g. /l., peripheral velocity V_g of 23 m. /sec., gas volocity w of 400 cu. m. /cu. m. hr. at 60-70°, $m = 4400x + 400$ and $n = -(0.13x + 0.24)$. The calcd. K_g agreed with the exptl. values within ±2-3%. The effect of the degree of oxidiation of NO to NO_2, q, on α was detd. at 30-45° with solns. contg. CaO 4-6 g. /l., C = 200-50 g. /l., at $V_g = 23$, and w = 300-20. With x = 2.2%, α increased from 69.8 to 82.1% as q increased from 30 to 70%; the N oxide content in the exit gases decreased from 0.371 to 0.258%. With x = 0.6% α increased from 62 to 73.2% as q increased from 32 to 68% and the concn. of N oxides in the exit gases decreased from 0.228 to 0.172%. The kinetics of the reaction was studied by the change in C of the partially recirculated soln. The results indicated that in a revolving absorber the rate of absorption of N_2O_3 and NO_2 were practically equal; this is attributed to the reactions $N_2O_3 + Ca(OH)_2 = Ca(NO_2)_2 + H_2O$ and $Ca(NO_2)_2 + 2NO_2 = Ca(NO_3)_2 + 2NO$.

98. Potasse et Engrais Chimiques (Quanquin, B., & Trimbach, H. inventors). Recovery of nitrogen oxides. Fr. Pat. 1 391 087 (Cl. C 01b) Mar. 5, 1965 (appl. Jan. 21, 1964); C.A. 63, 9510 h (1965).

A gas contg. $NO + NO_2$ 0.25% was scrubbed with lime water of 110 g. CaO/1. The effluent gas contained less than 0.023% $NO + NO_2$. The scrubbing soln. was treated with H_2SO_4 to ppt. $CaSO_4$ and recover the N oxides as 10% HNO_3.

99. Pozin, M.E., Kopylev, B.A., & Bel'chenko, G.V. Absorption of nitrogen oxides by milk of lime during bubbling and foaming conditions. Izvet. Vysshikh Ucheb. Zavedenii, Khim. i Khim. Tekhnol. 4, No. 1, 102-7 (1961); C.A. 55, 20344 g (1961).

N oxides were absorbed by milk of lime under foaming conditions at an extent of 5 times as great as during bubbling, and 10 times as great as in a packed column. For a content of 30-110 g. CaO/l. in the milk of lime, the degree of absorption practically did not change during the accumulation of the nitrite-nitrate salts (up to 200 g. /l.) in the soln. The degree of absorption during bubbling increased insignificantly on increasing the height of the column of liquid to 40-50 mm.; under foaming conditions, and increase in the rate of the liquid flow from 1 to 5 cu. m. /m. hr. resulted in an increase of the absorption degree on one shelf of the app. by 15-30% (relative). With an increase in the flow of the gas, the degree of absorption on one shelf decreased more during bubbling than under foaming conditions; this was due to the lower abs. values of the gas rate and a greater contact time of the phases. In the interval of linear gas rate from 0.5 to 2 m. /sec., the values of the absorption coeff. of an equimol. mixt. of N oxides at an initial concn. in the gas equal to 1%, was equal to 2000-3350 kg. N/cu. m. hr. atm. The insignificant variation in the degree of absorption depending on the concn. of milk of lime and on the accumulation of the nitrite-nitrate salts in soln. permitted realizing the absorption process with a rather high degree of absorption of the N oxides and obtaining relatively concd. nitrite-nitrate solns.. when the initial concn. of the N oxides was not very low. For low initial concns. of N oxides ($<0.5\%$), the regularities in their absorption changed sharply.

100. Schmidt, A., & Weinrotter, F. (to Osterreichische Stickstoffwerke AG). Removal of lower oxides of nitrogen from gaseous mixtures containing them. U.S. Pat. 3 034 853 (Cl. 23-2) May 15, 1962 (appl. Aug. 4, 1959).

Aq. suspensions of $Mg(OH)_2$ or $MgCO_3$ absorb NO and NO_2 to form $Mg(NO_2)_2$ and $Mg(NO_3)_2$. Upon heating, these compds. give up the NO and NO_2, thus regenerating the absorbent suspension. The regeneration is carried out at 140°-200° under pressure.

101. Vetrocoke Societa per azioni. Absorption of nitrogen oxides from the vent gas from nitric zcid-plant absorption systems. Ital. Pat. 513 953, Feb. 8, 1955; C.A. 52, 5764 f (1958).

The vent gas is passed through a packed tower where it is brought into contact with a suspension of lime in an aq. soln. of $Ca(NO_3)_2$ and $Ca(NO_2)_2$. Clear soln. obtained from a portion of the slurry leaving this tower is acidified with HNO_3 to convert the nitrite to nitrate. The N oxides formed are fed back to the front end of the main absorption system. The $Ca(NO_3)_2$ soln. from the acidifier is pumped either to

101. Cont'd. the appropriate tower in the main absorption system, in which case all the HNO_3 produced contains $Ca(NO_3)_2$; or is fed to a smaller absorption system fed with a portion of the gases from the NH_3-oxidation converter, in which case only a portion of the HNO_3 produced is contaminated with $Ca(NO_3)_2$. All the water required for the main absorption system is initially introduced with the lime suspension.

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102. Rodionov, A.I., Mishchenok, Yu. S., Klimov, A.P., & Bogdanov, E.A. Absorption of nitrogen oxides with a suspension of limestone. Tr. Mosk. Khim.-Tekhnol. Inst. 1963 (40) 74-77; C.A. 61, 6463 a (1964).

A gas contg. NO and NO_2 is scrubged with a slurry of finely ground $CaCO_3$ in an absorption column with 15 sieve trays. A foam layer is maintained over each tray. It was found that the percentage of absorption is increased by the increase in the concn. of nitrogen oxides in the gas and also by the increase in the oxidation of NO during absorption. The degree of this oxidation increases with the height of the foam layer over the seive tray. Within the range 16^o-58^o the degree of absorption of NO + NO_2 remained constant, other conditions being the same.

103. Zaklady Azotowe im. Pawla Findlera (Blasiak, E., & Jamiczek, W., inventors). Absorption of nitrogen oxides from dilute mixtures. Pol. Pat. 43 284, Aug. 30, 1960 (appl. Feb. 26, 1958); C.A. 57, 7075 f (1962).

Gases contg. small amounts of N oxides are passed through a bed of granular $CaCO_3$ (3-5 mm.) which is wetted by a spray of water which washes off the $Ca(NO_3)_2$ and $Ca(NO_2)_2$ formed on the surface of the granules.

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104. Bollinger, K. (to Colasit AG., Switzerland). Purifying air contaminated by acid or nitrous impurities. U.S. Pat 2 856 259 (Cl. 23-4) Oct. 14, 1958 (appl. Dec. 2, 1950).

The gas contg. N oxides is contacted with a mass of Fe_2O_3 supported on sawdust, arranged in two separate layers, one of which is irrigated with water. The gas first passes through the dry mass, then through the irrigated mass, so that the effluent gas contains no oxides of N.

105. Kainz, G., & Mayer, J. (Univ. Vienna). Absorption of nitrogen dioxide on manganese dioxide in C-H determinations. II. Mikrochim. Acta 1962, 241-8 (in German); C.A. 57, 50 b (1962).

The absorption of NO_2 by moist MnO_2 granules was found to improve with decreasing grain size. The water adsorbed on the MnO_2 granules served as additional absorbent. The efficiency of absorption decreases with temp. rise; as the temp. rises above 50^o the absorption product $Mn(NO_3)_2$ begins to decompose.

106. Purtseladze, Kh. G., Dzhikiya, S.I., Karumidze, Z.A., & Chkoniya, T.K. Absorption of nitrogen oxides by manganese hydroxide. Trudy Inst. Metal. i Gorn. Dela, Akad. Nauk Gruzin. S.S.S.R. 7, 239-247 (1956); C.A. 53, 8555 g (1959).

The results of lab. expts. on the absorption of N oxides at concns. of ∼0.3% and room temp. by Mn ores (Mn sponge, Mn carbonate, and pyrolusite) and paste-like Mn(OH)$_2$, contg. up to 65% water (with the addn. of wood shavings to reduce the resistance), showed that Mn ores quickly become deactivated; Mn(OH)$_2$ was the only compound tested which proved suitable for the absorption of N oxides. Mn (OH)$_2$ can be regenerated from the absorption product Mn (NO$_3$)$_2$ by the action of NH$_4$OH; as an alternate method, activated MnO$_2$ or Mn concentrates can be obtained by the thermal dissocn. of the nitrate.

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107. Fulweiler, W.H. (to United Gas Improvement Co.) Purification of gas from oxides of nitrogen. U.S. Pat. 2 031 410 (Cl. 23-3) Feb. 18, 1936 (appl. Sept. 16, 1933); C.A. 30, 2354 (4) (1936).

In the removal of N oxides by Fe sulfide, the efficiency is maintained by removing substantially all of the O$_2$ in the gas (suitably by the action of Cu at about 200°c.) before the gas is brought into contact with the Fe sulfide.

108. Ovcharenko, A.P., & Kovpakova, R.F. Purifying a gas of nitrogen oxides. U.S.S.R. Pat. 191 033 (Cl. C 10k) Jan. 14, 1967 (appl. Apr. 13, 1964); C.A. 68, 23238 b (1968).

The gas is purified by passing it through a packing of plane parallel steel plates. To increase the degree and rate of purification, freshly-deposited FeS is applied to the plates.

109. Ward, A.L., & Jordan, C.W. (to United Gas Improvement Co.) Gas purification. U.S. Pat. 1 976 704 (Cl. 23-3) Oct. 9, 1934 (appl. July 16, 1922); C.A. 28, 7441 (7) (1922); cf. U.S. Pat. 2 073 083 (1937); C.A. 31, 3244 (5) (1937).

The gas contg. about 35-52 g. NO per million cu.ft. and 0.5-0.6% O$_2$ is passed through a bed of spent "Lux" iron oxide contg. H$_2$S. The NO is entirely removed.

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110. Dita Orvam di Borgatti Tersilla. Removal of nitric oxides from the ozonized air emitted by ozonizers. Ital. Pat. 650 226 (Cl. C 01b) Dec. 10, 1962 (appl. Apr. 17, 1961); C.A. 67, 46966 f (1967).

Nitrogen oxides in the ozonized air are removed by filtering through a porous mass of alkaline material.

110a. Kainz, G. & Mayer, J. (Univ. Vienna). Very effective lead dioxide preparation for outside absorption of nitrogen dioxide in C-H analysis. Z. Anal. Chem. 191, 30-40 (1962); C.A. 58, 5040 e (1963).

PbO_2 with very high capacity for NO_2, suitable for use in elemental microanalysis, is prepared by alkaline oxidation of Pb^{++} with H_2O_2. The reaction of $KMnO_4$ with Pb^{++} in alkaline solns. yield active PbO_2MnO_2. The active part is $PbO(OH)_2$. NO_2 is adsorbed rapidly on the surface and slowly diffuses into the interior of the solid.

111. Kababadze, V.M., & Kakabadze, I.L. Absorption of nitrous gases in a dry method, with simultaneous production of mixed fertilizers. Soobshcheniya Akad. Nauk Gruzin. S.S.R. 18, No. 5, p. 549-556 (1957); C.A. 52, 13204 c (1958).

Absorption of N oxides from the waste gases of HNO_3 plants by dry oxides of Ca, Mn, or Mg is proposed as a means both of recovering the N oxides and of preventing pollution of the air by the waste gases. The reaction with CaO, e.g. is supposed to be $CaO + 2\ NO + 1.5\ O_2 = Ca(NO_3)_2$. The products are useful as fertilizers.

112. Kakabadze, V.M., & Kakabadze, I.L. Absorption of nitrogen oxides by a dry method. Tr. Gruz. Politekhn. Inst. 1959, No. 4, p. 43-50; C.A. 57, 11595 d (1962).

N oxides in waste gases are removed by passing the gas through hot beds of alkaline earth oxides using a series of several absorption columns. For example, the 1st and 2nd columns contain calcined dolomite at 300° and the 3rd through 8th columns contain calcined Mn carbonate ore. The spent absorbent materials are utilized as fertilizer materials.

113. Kitagawa, T. (to Kobe Steel Works, Ltd., Fukiai-ku, Kobe, Japan). Method of removing nitric oxide from gases. U.S. Pat. 3 382 033 (Cl. 23-2) May 7, 1968 (Jap. appl. Feb. 20, 1963).

Nitrogen oxides are removed from gases containing them by passing the gases through a porous medium impregnated with $FeSO_4$, $Na_2S_2O_3 + NaOH$, $NaHPO_4$, and similar compounds.

113a. Kobakhidze, A.G. The use of manganese carbonate ores in the chemical industry. Trudy Gruzin. Politekh. Inst. 1957, No. 6, p. 80-97 (in Georgian); C.A. 54, 8000 b (1960).

The $MnCO_3$ ores from Chiatura are calciumed at 900°-1000° for 15-30 min. to give a product contg. mainly MnO. This is used as an adsorbent in the purification of gases. It will adsorb H_2S, organic sulfur and nitrogen oxides such as in the tail gas of HNO_3 plants.

114. Ogg, Jr., R.A., & Ray, J.D. Method of recovering dilute nitrogen oxides from gaseous mixtures. U.S. Pat. 2 684 283, (Cl. 23-2) July 20, 1954 (appl. Sept. 21, 1950).

A gas contg. N oxides is mixed with O_2 and passed through a mass of Fe_2O_3 and Na_2O, the latter two being in 1:1 molar ratio, at a temp. in the range 300°-500° to form $NaNO_3$.

115. Perov, E.V. Absorption of nitrogen oxides by magnesium, strontium, and barium hydroxides. Tr. Novocherk. Politekhn. Inst. 121, 57-60 (1961); C.A. 61, 12696 g (1964).

N oxides were absorbed by solid $Mg(OH)_2$, $Ba(OH)_2 . 8H_2O$, and $Sr(OH)_2 . 8H_2$). Expts. with absorptionfrom mixts. contg. 0.25-1.0% of N oxides at 25-35° ($Mg(OH)_2$) and 15° (Sr and Ba hydroxides) showed that the process results in formation of nitrates and nitrites of these metals. Oxides adsorbed by the solid phase are easily swept out with air. From $Mg(OH)_2$ the salts may be sepd. by leaching with H_2O. In case of $Mg(OH)_2$ the rate of reaction is approx. the same at 25° and 35°. At a flow rate of the gas mixt. of 0.5 l./min. the satn. of the absorbent is achieved within 60-70 min. The absorbent utilization factor is then ~0.45. Reaction with Sr and Ba hydroxides (0.1 g. of absorbent at flow rate of the gas mixt. 0.5 l./min.) was completed within 30-40 min. The utilization of the solid mass is then 90% for $Sr(OH)_2 . 8H_2O$ and 48% for $Ba(OH)_2 . 8H_2O$.

116. Borok, M.T. Absorption of trace concentration of NO_2 by aqueous solutions of salts of aromatic amines. Zh. Prikl. Khim. 33, 2035-2042 (1960); C.A. 55, 24136 f (1961).

The rate of absorption (Q) and the degree of absorption (α), α = (initial concn. - final concn.)/initial concn., of NO_2 from a gas with initial concn. (C_i) 10^{-3}-10^{-2} mg./l. by benzidine in aq. AcOH (I) and by m-phenylenediamine in aq. HCl (II) were detd. in absorbers of 4 different geometric forms. In all absorbers, α decreased continuously as the gas rate (V) increased, but the relative rate of absorption, $q = dQ/dC_i = \alpha V$, passed through a max. q_o at V_o and decreased at $V > V_o$. The values of the consts. n, a, and b in the theoretical equation $\alpha = a\ (1 - bV^n)$ were calcd. from the exptl. α vs. V curves; n was practically independent of the structural parameters of the absorbers and of the concn. of I and II; n = 0.32. Apparently n was a function of the soly. of NO_2 in the liquid phase. For values of C_i from 0.002 to 0.012 mg./l. $\alpha \cong f(V)(1 + 0.001/C_i)C_i^{0.18}$, where the function f(V) was similar to the function $\alpha = a\,[(b/V^n) - 1]$.

117. Ganz, S.N., & Kuznetsov, I.E. Purifying gases by removal of nitrogen oxides. U.S.S.R. Pat. 186 985 (Cl. C 01b) Oct. 11, 1966 (appl. Mar. 19, 1965); C.A. 67, 13335 w (1967).

117. Cont'd. Nitrogen oxides are removed from gases by scrubbing the gases with an aq. solution of urea.

118. Maury, L.G., & Nahill, G.F. (to Hercules Powder Co.) Separation of solvated fixed nitrogen. U.S. Pat. 3 044 853 July 17, 1962 (appl. May 29, 1958); C.A. 57, 10776 e (1962).

An electron donor compound is separated from N compounds by contacting the donor compound with an oxidizing agent in the presence of a Lewis acid under conditions for converting N compounds to HNO_3. When NO_2 is present, a sufficient amount of H_2O in the contacting zone reacts with the NO_2 to form HNO_3 which is then separated from the solvent.

119. Maury, L.G., & Nahill, G.F. (to Hercules Powder Co.) Removing nitrogen oxides from fluids and nitrous acid. U.S. Pat 3 044 844, July 17, 1962 (appl. May 29, 1958); C.A. 57, 10780 b (1962).

The gases contg. small amounts of N oxides are passed through, or contacted in counter-current flow with a partially water-miscible liquid electron donor compound contg. 2-25% water. The temp. limits are 0-200°F. 80-100% of N oxides in the gases treated are thus removed. Examples of the electron donor compounds are: glycol ethers, alkyl phosphate, aryl phosphate, alkyl amines, alkyl sulfoxides, and alkyl phosphoramines.

120. Prokopovich, A.A., Balitskii, A.S., & Agafonov, E.T. Absorption of nitrogen oxides. U.S.S.R. Pat. 197 512 (Cl. B O1d b) June 9, 1967 (appl. June 29, 1966); C.A. 68, 88604 n (1968).

Bu_3PO_4 is specified as absorbent for nitrogen oxides.

121. Union Rheinische Braunkohlen Kraftstoff AG. (Hubenett, F., Dorffurt, H., & Nettesheim, G., inventors). Removal of nitrogen oxides from gases. Ger. Pat. 1 038 014 (Cl. 12 i) Sept. 4, 1958; C.A. 54, 17853 d (1960); cf. Ger. Pat. 1 104 494 (1961).

NO in gases is removed by first oxidizing it to NO_2. The latter is absorbed in an aq. soln. of a dialkyl sulfoxide and a dialkyl sulfone. The absorbent soln. is periodically regenerated.

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122. Giammarco, G. (to S.p.A. "Vetrocoke"). Removing nitrogen oxides from gaseous mixtures. U.S. Pat. 3 031 258, Apr. 24, 1962 (Ital. appl. Feb. 15, 1955); C.A. 57, 2520 f (1962).

The entire gas stream and contained total gums are heated to 90-150° for the release of all combined and occluded N oxides before passing the gaseous mixt. through equipment operated at superatm. pressure

122. Cont'd. and at sufficiently low temps. to maintain diene-class materials either in a liquid state or in a strongly concd. soln. in a liquid petrleum-derived solvent. The diene should boil at 35-45°. Cyclopentadiene is the most active diene. In the 2nd stage of the pressurized, low-temp. app., volatilized dienes are obtained from the gas stream for return to the 1st stage for addnl. removal of N oxides. Thus, 24,000 cu. m./hr. gas contg. 0.5 p.p.m. N oxides, compressed to 12 atm. was scrubbed at -40° bu 20 cu. m./hr. of kerosine contg. dienes, b. 35-40°. Approx. 2-4 cu. m./hr. was distd. by using hydroquinone to prevent polymerization of reaction products in the solvent.

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123. Szepesy, L., & Giona, A.R. (Univ. Rome, Italy). Elimination of nitrogen oxide in low concentrations by means of adsorption. Chim. Ind. (Milan) 47 (6), 588-92 (1965) (in Italian); Magy. Kem. Folyoirat 71 (9), 399-403 (1965) (in Hungarian); C.A. 63, 10725 g (1965); 64, 52 d (1966).

For the adsorption of NO from gas contg. NO in ppm. several adsorbents were investigated. They were ion-exchange resins, silica gel, molecular sieves and active C. Of these, active C showed best results. It was found that the displacement velocity of the adsorption zone is independent of concn. of NO and the distribution isotherm was linear in the range studied (0-16 ppm.) Isotherms at 20°, 50°, and 80° are shown.

124. Riese, W. Removal of nitric oxide from coke-oven gas transformed by thermal cracking. Brennstoff-Chem. 20, 301-8 (1939); C.A. 34, 6023 (4) (1940).

Expts. using chemical absorbents for the removal of 1-3 ppm. NO found in the coke-oven gas were unsuccessful. Adsorption of NO on activated C was found satisfactory. The C may be reactivated by heating at 300° in presence of steam. Silica gel was found not satisfactory as a NO adsorbent.

125. Smith, R.N., Lesnini, D., & Mooi, J. (Pomona College, Claremont, Calif.) The anomalous adsorptive properties of nitric oxide. J. Phys. Chem. 60, 1063-6 (1956); C.A. 51, 39 f (1957).

NO reacts readily with C surfaces at 0 and -78° to form gaseous N and C-O surface complexes. Thus, adsorption isotherms detd. at these temps. with C are fictitious: likewise, previous calorimetric measurements are heats of reactions, not heats of adsorption, for unknown amts. of NO. NO does not react with a C surface at -154°, and adsorption appears to be normal, although the adsorbed state is probably N_2O_2. NO also adsorbs normally on both porous and non-porous SiO_2 at 0 and -78°, but there is some reversible chemisorption in each case. NO may interact to some extent at -78° with the water bound in the SiO_2 gel.

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126. Solbakken, A., & Reyerson, L.H. (Univ. of Minnesota, Minneapolis). The chemisorption of nitric oxide by alumina gel at 0°. J. Phys. Chem. 66, 365-6 (1962); C.A. 56, 13573 i (1962).

The final equilibrium of the chemisorbed NO on Al_2O_3 gel was determined at the end of a 128-day period. The 228 mg. Al_2O_3 gel had adsorbed 2.56 mg. NO. The low transmission coeff. accounting for the slow chemisorption was confirmed by magnetic studies of the system.

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127. Mortland, M.M. (Michigan Agr. Expt. Sta., East Lansing). Nitric oxide adsorption by clay minerals. Soil Sci. Soc. Am. Proc. 29 (5), 514-19 (1965); C.A. 64, 7402 b (1966).

NO was chem. adsorbed on montmorillonite and nontronite when the exchange complex was satd. with certain transition metal ions. The ir data showed a no. of reactions depending on the nature of the satg. ion, including (1) coordination of NO as the mono or dinitrosyl complex, (2) formation of N_2O, and (3) formation of $(NO)^+$. The NO mol. was able to penetrate the interlamellar regions of Co montmorillonite or Co nontronite. On all other systems apparently only surface adsorption occurred. When air was admitted, all surface-adsorbed NO was immediately oxidized but interlamellar NO decreased at a rate dependent upon the diffusion of NO to the clay mineral surface. A product of oxidn. was found to be coordinated nitrile.

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128. Zarif'yants, Yu. A. (State Univ. Moscow). Properties of the surfaces of freshly cleaved graphite. IV. Adsorption and differential heat of adsorption of nitric oxide. Zh. Fiz. Khim. 38, 2655-8 (1964) (in Russian); C.A. 62, 3438 e (1965).

The mechanism of the reaction of NO with finely dispersed graphite, sp. surface 380 sq.m./g., was studied by adsorption and by magnetic susceptibility, x. At 100-600 mm. Hg, sorption was phys. At 5-100 mm. Hg, most NO adsorbed was irreversible. Sorption at 600 mm. followed by desorption 16 hrs. at 5×10^{-5} mm. left 4.8 micromoles/sq.m. as irreversibly adsorbed. The 2nd cycle was completely reversible. This was confirmed by x. The differential heat of adsorption during the initial period was 50-3 kcal./mole, whereas the heat of adsorption of the 2nd cycle was only 4 kcal./mole. Apparently the bond of NO was of the C–NO type. The presence of this bond was confirmed by the ir spectrum. The amt. of irreversibly adsorbed NO on a completely oxidized graphite surface was 2.2 micromoles/sq.m. suggesting a covalent bond of the –O–NO type.

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129. Briner, E., & Sguaitamatti, B. The recovery of nitrogenous gases by adsorption. I. Adsorption of nitric oxide by silica gel. Helv. Chim. Acta 23, 1216-1231 (1940); C.A. 35, 2051 a (1941).

Adsorption of NO on silica gel was studied at -78°, 0°, and 50°. The data were compared with those for O_2 and CO_2.

130. Briner, E., & Sguatamatti, B. The recovery of nitrogenous gases by adsorption. III. Recovery of nitric oxide from silica gel. Helv. Chim. Acta 24, 421-434 (1941); C.A. 35, 7788 (3) (1941).

The adsorption of NO from air by silica gel increased with decrease in temp. and with increase in moisture content of the air. A mechanism is proposed leading ultimately to the formation of HNO_3 on silica gel. Upon heating, the desorbed gas mixt. contains both NO and N_2O_4. Recovery is nearly 100%.

131. Kazakova, E.A., Khiterer, R.Z., & Bomshtein, V.E. Apparatus for purifying nitrose waste gases with fluidized silica gel circulating in an adsorber-desorber system. Khim, Prom. 44 517-520 (1968); Brit. Chem. Eng. 14, 667-8 (May 1969); C.A. 69, 79960 u (1968).

Waste gases from HNO_3 manuf. contg. 0.2-0.3 vol. % of NO + NO_2, were cooled to 0°, the condensed HNO_3 was sepd., and the gases were brought in contact with a countercurrent stream of silica gel particles (0.2-3.0 mm. in diam.) fluidized bya ir. As a result, the concn. of N oxides in the waste gases was reduced to 0.04-0.05 vol. % and the gases were released to the atm. After satn. of the silica gel with N oxides (to 50-60% of its capacity), it was moved to a desorber where it was regenerated by contact with dry steam at 180-90°, and then returned to the absorption tower. Gradual decrease in the particle size of the silica gel occurred with time. Pilot-plant equipment for continuous fluidized-bed adsorption-desorption of the N oxides is described.

132. Kuznetsov—Fetisov, L.I., & Krasnyi, E.B. Adsorption of nitric oxide. Trudy Kazan. Khim.-Tekhnol. Inst. im. S.M. Kirova 1958, No. 22, 106-116, C.A. 53, 21029 e (1959).

Static activity of local adsorbents towards NO is investigated gravimetrically at 10, 25, and 40° and equil. pressures of 100-760 mm. Five to 6 cycles of detns. are made for each adsorbent at const. conditions by noting the elongation of a quartz or Mo-glass spiral at sorption equil. (the error is 1-5%). SiO_2 gel, Al_2O_3 gel, Fe_2O_3 gel, SiO_2 gel copptd. with $Ni(OH)_2$ gel and $Cu(OH)_2$, carboalumino gel, and carbosilica gel, all having 2.5-4 mm. particle size, were made in the lab. Com. adsorbent SiO_2 gels, KSM, MSM, KSK, and a silica gel contg. Al_2O_3 ShGSG; and bauxite from south Ural of 2.5-4 mm. particle size are used as adsorbents. Carboalumogel, SiO_2 gel copptd. with Ni()H)$_2$ gel and $Cu(OH)_2$ andSiO_2 gel KSM possess the max.

132. Cont'd. static activity, each at different temps. in the order listed (carboalumogel and SiO_2 gel copptd. with $Ni(OH)_2$ gel have the max. activity at all temps.) At increased temps. the adsorption value of all adsorbents decreases in 2 intervals of 10-25° and 25-40° by 1.4-2 times in each. The isotherms of adsorption are S-shaped indicating the possibility of multimol adsorption. The best conditions of desorption are 300° and evacuation to 10^{-5} mm. and give 98-9% desorption. Incompleteness of desorption and formation of color on the surface of the adsorbents reveals the possibility of chem. reactions with H_2O of constitution to give higher oxides, HNO_3, and chemisorbed complexes. The Freundlich adsorption isotherm equation can be used as an interpolation formula for the exptl. results with all adsorbents. This was checked graphically. The Langmuir equation is inapplicable for this purpose. The calcd. apparent activation energy E_{10-25° of NO adsorption on SiO_2 copptd. with $Ni(OH)_2$ gel is 1940 cal./mole, bauxite 2356, ferrogel 3019, carboalumogel 4514 and SiO_2 gel KSM 7100; and E_{25-40°, 2244, 2204, 2604, 3669, and 9533, resp., at 760 mm. pressure and 10, 25, and 40°. Energy of activation influences the adsorption of gaseous substances.

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133. Brenman, J.A. (to Socony Mobile Oil Co.) Removal of nitrogen oxides from combustion gases. U.S. Pat. 3 015 369, Jan. 2, 1962 (appl. May 23, 1960); C.A. 56, 9715 f (1962).

NO in exhaust gases is removed by passing the gases through a hot bed of 13X molecular sieve. 2 examples are given. (1) At 420° and space velocity 31,200 per h., the NO content of a N_2 gas was reduced from 0.55 down to 0.13 mg./l. (97 ppm. by vol.) after 3 h. (2) At 400° and space velocity of 3000 per h., the NO content was reduced from 0.88 down to 0.02 mg./l. (15 ppm. by vol.) after 1 h. of operation.

134. Chachulski, J., Kornblit, L., Kruszka, F., Kcczorowica, B., & Woszek, B. (Sodium plant Inowroclaw, Poland). Type 5A molecular sieves of Polish production. Chemik (Gliwice) 18, 252-5 (1965) (in Polish).

A synthetic zeolite was prepared having an approximate formula 0.7 CaO. 0.3 Na_2O. Al_2O_3. 2 SiO_2. It was found to absorb readily at room temp. 28 different gases and vapors including CO_2, COS, CS_2, Cl_2, CH_4, C_2H_2, and NO.

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135. Baranov, A.V. Okhramovich, A.E., & Pashchenko, P.A. Adsorption of nitrogen oxides by activated carbon. Trudy Dnepropetrovsk Khim.-Tekhnol. Inst. 1958, No. 6, p. 35-65; C.A. 55, 7982 e (1961).

Factors affecting the dynamic capacity of activated C (brand Bay) and the time before N oxides passed through the adsorbent that were studied were temp., concn. of N oxides in the gas mixt., linear and total velocity of the gas mixt., depth of the layer, av. size of granules, and moisture content of the absorbent. Activated C adsorbed N oxides well. When it was used for collecting N oxides from tail gases from the production of HNO_3, the vol. of the tower for acid absorption could be decreased, and the concn. of N oxides in the gas entering the first tower increased.

136. Baranov, A.V., & Okhramovich, A.E. The desorption of nitrogen oxides from activated carbon. Nauchn. Tr. Dnepropetr. Khim. Tekhnol. Inst. 1961, No. 12, Pt. 2, p. 185-8, C.A. 57, 15861 e (1962).

The kinetics of desorption of N oxides from activated carbon were studied at 100-200°, both in. vacuo and in a flow of air. The total desorption was measured by absorbing the gas in 0.5N NaOH, and the reaction was followed by weighing the tube contg. the carbon at 5-min. intervals. In an air flow of 10 ml./min. the rate of desorption at $\leq 100^\circ$ was very low. Thus, in 2 hrs. at 100°, 80% desorption was observed. The rate of desorption increases with increasing temp. At 125° desorption was 90% in 1 hr.; at 150° 95% in 1 hr.; at 175° 100% in 30 min.; at 200° 100% in 10-15 min. The activity of the carbon was not lost after repeated sorption and desorption. CO_2 appeared in the desorbed gases as a result of the action of the N oxides on the carbon. The rate of attack depended on temp. The kinetics of desorption in vacuo were studied at 100 and 125°. The rate of desorption in vacuo is much greater than in a low rate of air flow at the same temp. Thus, at 100°, 93% was desorbed in 30 min. in vacuo, and only 78% in 2 hrs. in an air flow. Most of the desorption occurred in the first 15 min. The degree of desorption in vacuo at 125° was equiv. to that in a flow of air at 175°.

137. Ganz, S.N. (Chem.-Technol. Inst., Dnepropetrovsk). Adsorption of nitrogen oxides by solid adsorbents. I. Zh. Prikl. Khim. 31, 138-140 (1958); C.A. 52, 9534 a (1958); English transl, available at Chemico Library.

The absorption of NO + NO_2 by solid absorbents at 18-20° was investigated. A 0.3% gas (NO 60 + NO_2 40%) was passed at 1000-2000 cu. m./cu. m. hr. at linear velocities from 0.024 to 0.048 m./sec. through a packed tower. The rate of absorption and the

137. Cont'd. capacity decreased in the following order: activated C > Al silicate > SiO_2 gel > MnO_2 > CuO > MnO_2 60 + CuO 40%. Because of the catalytic oxidation and the formation of HNO_3, desorption was possible only above 300°. The most stable absorbent was Al silicate.

138. Kurita Kogyo KK. Adsorption of nitrogen oxides. Japan Pat. 23 925 (1963); cf. Chemiker-Ztg. /Chem. Apparatur 89, 632-635 (1965).

A gas contg. 0.2% nitrogen oxides was passed over active C made from coconut shell to remove 95-98% of the N oxides. The active C was regenerated by washing with water followed by drying.

139. Lozhkin, A.F., & Subochev, N.L. Recovery of nitrogen oxides from lean gases by activated carbon in a moving bed. Sb. Nauch. Tr., Perm. Politekh. Inst. No. 18, 61-74 (1965); C.A. 66, 20533 s (1967).

The adsorption of N oxides from gases contg. low concns. of the N oxides by granulated activated carbons of grade KAD and AG in a fixed bed and in a moving bed was studied. The adsorption capacities of the KAD and AG carbons were equal and depended on the degree of oxidn. of the N oxides in the gas; the higher the degree of oxidn., the higher the adsorption capacity, all other conditions being equal. The possibility of detg. the linear transporting velocity of the carbon in a hypersorber by using data on the movement of points of equal concn. in a fixed bed was studied. During the thermal regeneration of the spent carbons, dissocn. of NO_2 into NO and O takes place on the surface of the adsorbent. As a result, some of the carbon is lost by the formation of CO_2. For each adsorption-desorption cycle, the combustion losses of KAD and AG were ~0.5 and 0.4% of the inital wt., resp.

140. Ruhrchemie AG (Rottig, W., inventor). Separation of nitrogen oxides from residual gases from nitric acid production. Ger. Pat. 1 040 003 (Cl. 12 i) Oct. 11, 1958; C.A. 54, 25645 b (1960).

The gases are treated at 5°-40° with activated C and passed over alkaline earth oxides and/or hydroxides or carbonates after saturating with water. The coefficient of absorption is 80-90%.

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141. Ganz, S.N. (Chem.-Technol. Inst., Dnepropetrovsk). Adsorption of nitrogen oxides by solid adsorbers. II. Adsorption by aluminum silicate sorbents. Zh. Prikl. Khim. 31, 360-8 (1958); C.A. 52, 13204 a (1958).

The degree of adsorption K' of dry NO + NO_2 and the degree of oxidation K'' of NO by Al silicate at 18-20° decreased with the gas rate w and increased with the concn. of NO + NO_2 in the gas (0.5-2.15%). The

141. Cont'd. rate of adsorption, kg. /cu. m. hr., and the coeff. of adsorption, kg. /cu. m. hr. atm., increased with w and passed through a max. at w = 600-900 cu. m. /cu. m. hr. Apparently Al silicate acted as a catalyst of NO oxidation. With moist gases K' decreased as the H_2O vapor in the gas increased. In the temp. range from 12 to 42° with w = 500, H_2O in the gas 3. 1%, and $NO + NO_2 = 1.38\%$,K'' was 96-8% and K' decreased from 97% (in dry gas) to 78%. K' decreased as the temp. increased from 45 to 60°. Desorption with N at 160-500° yielded HNO_3. Complete desorption was obtained with $NO + NO_2$ gases at 300°.

142. Kulcsar, G. J., & Vodnar, I. (Univ. Babes-Bolyai, Cluj, Romania). Adsorption of nitrogen dioxide on aluminum silicate. I. Adsorption capacity of activated kaolin. Studia Univ. Babe-Bolyai, Ser. Chemia 9 (1), 47-53 (1964); C. A. 61, 15386 d (1964).

The kaolin used contained 98% $Al_2O_3 . 2SiO_2 . 2H_2O$. It was activated by the Kopylov method, resulting in a sp. surface of 48. 5 sq. m. /g. The gas used to measure the adsorption capacity contained 4. 64% NO_2. The "degree of adsorption" was found to be 20. 59% at 20. 8°. Repeated adsorption and desorption caused the activity of kaolin to decrease (to 75. 33% of its initial value after 5 cycles).

143. Kulcsar, G. J., Vodnar, I., Lengyel-Szabo, Gy., Boejthe, P., & Zete, Z. (Univ. Bables-Bolyai, Cluj, Romania). Adsorption of nitrogen dioxide on aluminum silicates. II. Studia Univ. Babes-Bolyia, Ser. Chem. 11 (1), 79-84 (1966) (in Romanian); C. A. 65, 17734 (1966).

The adsorption of NO_2 on these kaolins was studied by a previous method (CA 61, 15386 d). The NO_2 was generated by bubbling SO_2 through a 68% soln. of HNO_3 at 80°. The apparent adsorbent vol. was 35 cc. and the air was passed at a const. rate of 4450 cc. /hr. The initial NO_2 concn. in the air was ∼12%. The degree of adsorption of the NO_2 is given as a function of the initial NO_2 content of the kaolin at 25-120°. The degree of adsorption decreased with increasing temp. and increasing NO_2 content of the kaolin. The amt. of NO_2 retained on fresh adsorbers at 25° was I 0. 27 and II 0. 42 millimoles NO_2/g. adsorber. In the two cases, the amt. of NO_2 adsorbed from the gas was I 95 and II 99%, but only ∼50% for kaolins already contg. I 0. 18 and II 0. 30 millimoles NO_2/g. adsorber. The degree of adsorption decreased sharply from 20° to 40°. This was attributed in part to the displacement of the equil. $2NO_2 \rightleftarrows N_2O_4$. Despite this sharp decrease of adsorption with temp., the retention of NO_2 by fresh kaolins at 120° was still I 55. 4 and II 66. 4% of the amt. present in the gases. The total adsorption capacity of the kaolins decreased from I 0. 12 and II 0. 35 millimoles NO_2/g at 25° to I 0. 05 and II 0. 055 millimoles NO_2/g. at 120°. Regenerated kaolins lost 34% of the total adsorption capacity after the first regeneration and 11% in addn. after the 2nd.

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144. Gordunkel, V.E., Kazakova, E.A., & Chernyavskaya, M.K. Purification of exhaust gases. U.S.S.R. Pat. 129 193, June 15, 1960; C.A. 55, 3039 f (1961).

Exhaust gases contg. approx. 0.3% N oxides are cooled to about 0°C. and passed through miltistage fluidized beds of silica gel. The adsorbed N oxides are then desorbed from the silica gel by heating the gel and blowing air through the beds.

145. Kazakova, E.A., Chernyavskaya, M.K., & Nizhegorodova, N.V. Enrichment of dilute nitrous gases by adsorption in a fluidized bed. Khim, Prom. 1962, 506-512; C.A. 58, 3114 f (1963).

The enrichment of dil. nitrous gases by a modified Wisconsin process (Ermence, CA 51, 1557 a) was studied in the lab. The modifications introduced were: NO_2 was adsorbed on finer silica gel particles than in the original process. The catalytic oxidn. of the NO to NO_2 was carried out in a fluidized bed at -10° instead of at -50°, the adsorption of NO_2 on the lower trays was non-adiabatic, and the desorption process was also carried out in a fluidized bed. The NO_2 content in the enriched gas was 30-40% as compared with 2.5% $NO + NO_2$ in the raw material. Among the silica gels studied brand ASM had the highest adsorption capacity, 45 g. NO_2/100 g. adsorbent at -11° and 150 mm. The equil. concn. of H_2O on the adsorbent was close to the equil. H_2O concn. in the gas at the exit of the fluidized bed; equil, adsorption of the H_2O was obtained with bed thicknesses below 50 mm. The capacity of the silica gel increased with increasing H_2O content in the raw gas showing that part of the NO_2 was absorbed on water on the silica gel. The effect of gas velocity (within the range 0.13-0.30 m./sec.) on the degree of adsorption of the NO_2 was insignificant. i.e., there exists a rate-controlling interal diffusion process. Complete desorption of the NO_2 was obtained by blowing air for 15-20 min. at 180-200°. Expts. on a pilot-plant column showed that the amt. of silica gel needed to adsorb 1 g. NO_2 varied from 7 to 40 g. within the temp. range 0-20°. The presence of NO reduces the degree of adsorption of the NO_2; this redn. is, however, slight and by using the combined NO_2 adsorption-NO oxidn. method, the overall energy consumption is practically equal to that in the adsorption of NO_2 from NO-free gases.

146. Krasnyi, E.B., Kuznetsov-Fetisov, L.I., & Rozenberg, G.I. (Khim.-Tekhnol. Inst., Kazan). The adsorption of low concentrations of nitrogen dioxide-nitrogen tetroxide under dynamic conditions. Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol. 6, 802-5 (1963); C.A. 60, 8669 e (1964).

146. Cont'd. The sorption characteristics of a com. SiO_2 gel (I) designated as KSM were compared with those of a synthetic NiO-SiO_2 gel (II) for removal of low concns. (0.5-1%) of NO_2+N_2O_4 from air. Apparent d. of I was 1.388, that of II was 1,236; sp. surface of I was 654 sq. m./g., that of II was 448. Grain size of I was 2.7-7 mm. Adsorptions were carried out at 25° in a 14 mm. diam. U-tube with a bed depth of 40 cm. and a gas velocity of 1 m./min. Desorption was conducted by passing air through the U-tube at 350°. For each gel, adsorption-desorption cycle was repeated several times with similar results. Time to break-through (indicated by coloration of KI-starch soln. through which effluent air was bubbled) was 51-73 min. for I and 531-737 min. for II. At break-through I and II had adsorbed 0.43 and 5.7 g. N oxides/100 g. gel, resp., from air contg. 1% N oxides. Adsorption isotherm of II was S-shaped, whereas that of I was a smooth curve.

147. Krasnyi, E.B., & Kuznetsov-Fetisov, L.I. Investigation of the adsorption and desorption of NO_2+N_2O_4 on technical silica gels ASM and No. 6. Tr. Kazansk. Khim.-Tekhnol. Inst. No. 30, p. 223-239 (1962); C.A. 60, 3515 b (1964).

Two tech. SiO_2 gels, ASM and No. 6, were structurally characterized according to 9 phys. properties: apparent d., true d., total porosity, total pore vol., max. adsorbed vol., sp. surface, effective radius of pores at max. of distribution curve, pore radius, and particle diam. The amt. of structure H_2O for ASM and No. 6 is, resp., 5.66 and 4.53%. These SiO_2 gels belong to the 3rd structural type (uniform, fine pore adsorbent) according to the classification made by Kiselev (CA 43, 6033 i). Adsorption and desorption isotherms of NO_2+N_2O_4 on SiO_2 gel ASM and No. 6 were obtained at −1, 0, 10, 20, 40, and 100° and relative pressures from 0 to 1. The activity of the gels is independent of temp. in this pressure range. At const. equil. satn. pressures, the activity increases with temp. decrease. The dependence of activity on a change of equil. and relative pressure at const. temp. is the same for both gels. The adsorption isotherms are of the Langmuir type and can be described by the B.E.T. equation in the relative pressure range from 0.07 to 0.32. The NO_2+N_2O_4 was proved to be monomol., adsorbed and for complete adsorption of low concns. of NO_2+N_2O_4 it is necessary to use adsorbents of the 3rd structural type with pore diam. of 20-22 A. Indirectly a partial chemisorption arises from interaction of the N oxides with the OH groups of the silicic acid to form stable chemisorbed complexes. The adsorptive properties of SiO_2 gels depend on 2 factors: structural (pore size) and chem. (degree of hydration of the gel surface).

148. Mizukami, S. Carbon and hydrogen determination. Hydroxyl-amine sulfate as an adsorption agent for oxides of nitrogen. J. Pharm. Soc. Japan 76, 1216 (1956); C.A. 51, 945 i (1957).

Adsorption of NO_2 (in the case of NO. it is first oxidized to NO_2) is effected by using SiO_2 gel contg. 30% $NH_2OHH_2SO_4$. A satisfactory result was obtained in the analysis of C and H in picric acid, $MeNO_2$, and dicyandiamide, etc.

149. Peters, M.S. (Univ. of Ill.) Stop pollution by nitrogen oxides. Chem. Eng. 62, May 1955, p. 197-200.

Efficiencies of removal of NO_2 and N_2O_4 from air by absorption by water and adsorption on silica gel were compared exptly. Results indicated that the highest efficiency may be obtained from water absorption using porous glass as gas-bubble producer. This system requires a higher pressure drop and a lower gas rate than corresponding systems of water spray tower, packed column, bubble-cap tower, and dry silica gel. The removal efficiencies of the last two systems were found next highest. Data are agiven.

150. Sundaresan, B.B., Harding, C.I., May, F.P., & Hendrickson, E.R. (Univ. of Florida, Gainesville). Adsorption of nitrogen oxides from waste gas. Environ. Sci. & Technol. 1, 151-6 (Feb. 1967); Nitrogen (London) No. 48, July/Aug. 1967, p. 38; C.A. 66, 88456 z (1967).

A systematic study was carried out of the adsorption of N oxides on silica gel and commercial zeolite. It was found that the zeolite is more efficient than silica gel. A simulated HNO_3 plant tail gas was used in the experiments The input gas contained 1800 ppm. N oxides calcd. as NO_2 and the exit gas contained less than 10 ppm. of N oxides with a given cycle which has a continuous adsorption period of up to 3 h., although it is considered that a N oxides concn. of 200 ppm. in the HNO_3 plant exit gas is permissible. The N oxides were desorbed from zeolite by action of hot air or steam. A treatment for 30 min. gave an 80-85% recovery of N oxides, of which 1/4 was in the form of enriched N oxides and 3/4 in the form of a weak acid contg. about 20% HNO_3. The scheme of removal and recovery of N oxides by adsorption was considered feasible for full-scale HNO_3 plants.

151. Veal, D.J. (to Phillips Petr. Co.) Removal of nitric oxide from gas streams. U.S. Pat 3 050 363 (Cl. 23-157) Aug. 21, 1962 (appl. July 28, 1958).

Silica gel with additions of I_2O_5 or CrO_3 was found to be effective to adsorb NO and NO_2. The NO is oxidized to NO_2 in the adsorbed state.

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152. Anon. -1966. Process cleans up nitric tail gas. Chem. Eng. News 44, July 4, 1966, p. 13.

Dr. C.I. Harding, Gainsville, Florida, and associates propose to recover N oxides in 0.1-0.4% range in the tail gas of HNO_3 plants by adsorption by zeolite.

153. Anon. -1967. Removal of nitrogen oxides in tail gases by silica or zeolites. Nitrogen No. 47, May-June 1967, p. 36.

Removal of nitrogen oxides (NO and NO_2) from nitric acid plant exit-gases has been investigated by Dr. Harding and co-workers at the University of Florida. Volumetric composition of the tail gases studied was:

	% Content
Nitrogen oxides (NO + NO_2)	0.1-0.4
Oxygen	3-4
Water	1
Nitrogen	95

It has not proved economic to recover these oxides of nitrogen and to recycle them using absorption equipment. Nevertheless, the NO + NO_2 content is such that it constitutes a pollution problem. Dr. Harding and his co-workers have been investigating--and the results are reported to be successful-- an adsorption-desorption cycle of these nitrogen oxides on silica or zeolites. In operation at one nitric acid installation at 40°C, passage through a molecular sieve (in preference to silica gel) reduced the tail gas content to 0.001% oxides of nitrogen after 3 h. and then to 0.02% after 5h 20 min and to 0.8% after 7 h. The zeolite is regenerated by injection of steam or air at 160°C. The nitrogen oxides are removed in a concentrated state and are recycled. It is estimated that the zeolites will be able to be employed for 2,000 cycles, but this is not yet definitely determined. Application of the technique and process on a large scale is expected to permit an increase in production of 4 to 5 tons in a 300 tons p.d. nitric acid unit.

154. Krasnyi, E.B., Musin, T.G., Piguzova, L.I., & Nikolina, V. Ya. Adsorption and desorption of NO_2+ N_2O_4 on synthetic acid resistant zeolites. Khim. Prom. 42 (7), 523-4 (1966) (in Russian); C.A. 65, 16091 g (1966).

The isotherms of adsorption and desorption of mixed NO_2 and N_2O_4 on 5 kinds of synthetic zeolite and technical silica gel were determined. The adsorption capacity of the 4 of the 5 zeolites tested was 3.7-9.0 times as great as that of silica gel.

155. Piguzova, L.I., Nikolina, V. Ya., Dubinin, M.M., & Shishakova, T.N. Acid resistance of the synthetic zeolite erionite. Khim. Tekhnol. Topliv i Masel 10 (10), 32-34 (1965) (in Russian); C.A. 64, 6126 f (1966).

Synthetic erionite, ($0.5K_2O.0.4Na_2O.Al_2O_3.6.6SiO_2.5.5H_2O$) was treated with 0.006-3N HCl solns. at 96-98° for 1 hr. The zeolite was washed, and its capacity for H_2O and $NO_2+N_2O_4$ was detd. At pH $\sim$2.1-.24, the zeolite structure is preserved. After treatment with 0.1 N HCl, the capacity for H_2O and the crystal lattice are essentially unchanged. The substitution of Na^+ and K^+ with H^+ does not destroy the crystal lattice. The zeolite was studied in the H-form in the batch adsorption-desorption of $NO_2+N_2O_4$. At small concns., the adsorption capacity of the zeolite is higher than that of silica gel. After 8 cycles of adsorption-desorption of $NO_2+N_2O_4$, no changes in the adsorption properties and structure of the zeolite were found.

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156. Rizaev, N.U., Nabieva, Z.M., Saldadze, K.M., & Merenkov, K.V. Adsorption of nitrogen oxides from exhaust gases by anion-exchange agents. Uzb. Khim. Zh. 10 (5) 70-72 (1966); C.A. 66, 49045 v (1967).

Anion-exchange agents were used for the elimination of N oxides. With the anion-exchange agents AN-23 and AN-25 in the 1st period, 60% of the N oxides was adsorbed from the exhaust. The adsorption of NO_2 requires its transformation to HNO_3 using moisture from the exchange agent. Of 3 moles NO_2, 2 moles are transformed to HNO_3 and 1 to NO. The exhaust gases studied contained 0.2-0.4% N oxides. The level after passing the exchange agent was 0.08-0.16%. The desorption of the anion by 0.2-0.5 N NaOH completely restores the adsorption capacity of the exchange agent. AN-23 and AN-25 have a capacity of NO_3^- adsorption which is 5-6 times that of silica gel. The exchange agents have no catalytic effects on the oxidn. of NO to NO_2. The industrial samples of AN-23 and AN-25 were washed free of Fe ions by 5% HCl. The excess Cl^- was removed with H_2O. The agents in the OH form were obtained by the equation $RCl + NaOH \rightleftharpoons ROH + NaCl$. For expts. under dynamic conditions batches of 10-15 g. were prepd and allowed to stand with H_2O for 3-4 hrs. for swelling. After that the exchange agents were poured into the column together with H_2O. The exchange agent AN-25 is the best sorbent for sorption and desorption of N oxides from exhaust gases.

157. Tuerkoelmez, S. Synthetic resin ion-exchanger for eliminating obnoxious odors through exchange adsorption. Wasser Luft Betrieb 9 (11), 737-743; (12), 912-6 (1965) (in German); C.A. 65, 12768 e (1966).

For the purification of industrial waste gases, polymer resins can be used as ion exchangers which will adsorb nitrous gases, such as NO, NO_2, N_2O_4 and N_2O_3. This adsorption may be coupled with splitting of certain molecules by saponification, hydrolysis, or other reaction mechanisms.

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158. Pozin, M.E., Kopylev, B.A., Bel'chenko, G.V., & Obruba, P. Cleaning gases of nitrogen oxides with the production of a fertilizer-nitrated peat. Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol. 9 (2), 276-9 (1966); C.A. 65, 11287 f (1966).

In tests conducted in a 38 mm. diam. column, at 18-20°, peat from the Leningrad region (52% moisture) absorbed 60% of the NO_2 contained in air with 0.2% NO_2 over a 6-hr. period. The air was passed through at 0.1 m./sec. (2255 $m.^3$/ton-hr.). At 0.2 m./sec., (13550 $m.^3$/ton-hr.), NO_2 removal efficiency dropped from 45% initially to 20% after 3 hrs. Removal efficiency was little affected by variation in initial NO_2 concn. from 0.1 to 0.3%. Removal of NO_2 from air varied from 32% for an initial concn. of 0.1%, to 20% for an initial concn. of 0.3%, at a linear velocity of 0.1 m./sec. (2255 $m.^3$/ton-hr.). Other samples of peat showed somewhat better sorption characteristics. It is proposed that following sorption of N oxides, the peat be treated with NH_4OH. It appears possible thereby to produce a peat contg. 11% N in this manner for use as a fertilizer.